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EGG ALBUMIN.

By Thomas B. Osborne.

HOPKINS has recently shown[1] that the crystallization of egg albumin is greatly facilitated by the addition of acetic acid to the half saturated ammonium sulphate solution. I have found that crystallization is thus promoted, because the crystallized egg albumin is a compound of the protein substance with acid.

When egg white is first mixed with half saturated ammonium sulphate solution an alkaline reaction towards litmus can be detected and a decided odor of free ammonia develops. After this solution has stood for some hours, all evidence of free ammonia disappears and the solution is then perfectly neutral to litmus and continues neutral during the gradual separation of the albumin. The deposited substance, whether in the form of spheroids or of crystals, when filtered out and dissolved in water, reacts distinctly acid with litmus, as well as with phenolphthalein.

In order to obtain the albumin in crystals, it has heretofore been necessary to precipitate it several times, evidently because, during the earlier evaporations, an insufficient amount of acid

[1] *Jour. Physiology*, **23**, 131.

is formed to produce the crystalline compound. It is also for this reason that, if acetic acid be added as Hopkins directs, the albumin is obtained completely crystallized by a single precipitation, and that too without any concentration by evaporation.

I have found that if, instead of acetic acid, a molecularly equivalent quantity of hydrochloric acid be added, the separation takes place even more quickly and, so far as my experience has as yet gone, within a short time is more complete than with acetic acid during the same time. Thus, I prepared from two portions of 1500 cc. each of perfectly fresh egg white a quantity of crystallized egg albumin by aid of each of these acids, with the following results :

After adding to one-half of the egg white, acetic acid in the proportion and manner directed by Hopkins, and a molecularly equivalent quantity of hydrochloric acid mixed with 300 cc. of half-saturated ammonium sulphate solution to the other half, the two solutions were set aside to deposit albumin. After three hours a very large crystalline precipitate had separated in the portion with hydrochloric acid. This precipitate was then filtered out, but the portion with acetic acid was allowed to stand for twenty-four hours, because the separation appeared to be much less than that in the hydrochloric solution.

These two precipitates were each twice recrystallized, freed as completely as possible from mother-liquor, by pressing out with filter-paper, dissolved in water, and the solutions dialyzed for ten days, until wholly freed from sulphate, when they were filtered clear and evaporated at about 50°. The residue left by the acetic acid solution, A.1, weighed twenty-nine grams ; that from the hydrochloric acid, H.1, fifty-nine grams.

The filtrates from the several crystallizations of these two preparations yielded a second crop of completely crystallized albumin ; that from the acetic acid solution, A.2, weighing forty-three grams ; that from the hydrochloric acid solution, H.2, seven and nine-tenths grams. Similarly, from the mother-liquors from these preparations, two other entirely crystalline products were obtained, weighing respectively, A.3, eight grams and H.3, four and nine-tenths grams. From the finally remaining acetic acid solutions another preparation separated, consisting wholly of spheroids, A.4, which weighed nine and one-tenth grams.

There were thus secured from 1500 cc. of egg white, by adding acetic acid, 80 grams of wholly crystallized albumin, and from 1500 cc., with hydrochloric acid, 73.2 grams, or 5.30 and 4.90 grams respectively per cubic centimeter of egg white.

The crystallized albumin, like all the other protein preparations which I have as yet examined, is a compound of a protein substance with an acid. In order to neutralize to litmus and to phenolphthalein the solutions of one gram of each of these preparations of albumin, it was necessary to add the following quantities of decinormal potassium hydroxide solution :

	A.1.	A.2.	A.3.	A.4.	H.1.	H.2.	H.3.
To phenolphthalein	2.05	2.30	2.30	2.35	2.05	2.25	2.20
To litmus	1.30	1.60	1.65	1.55	1.30	1.60	1.50
Difference	0.75	0.70	0.65	0.80	0.75	0.65	0.70

If, as pointed out in another paper, the molecular weight of the protein substance is about 15,000,[1] one gram would react with 0.67 cc. of a decinormal solution, a quantity nearly equal to the difference in acidity shown by these two indicators. Three molecules of acid reacting with one of albumin would be equal to two cc. of decinormal solution per gram of albumin, a quantity in very close agreement with that found for the two fractions constituting the greater part of all the albumin, A. 1, and H. 1., and which also differs but little from that required to neutralize one gram of all the other fractions.

When the albumin, dissolved in water, was neutralized with decinormal potassium hydroxide, the solution evaporated to dryness and the proteid matter burned off, an ash was left containing potassium carbonate almost molecularly equivalent to the acid of the albumin originally neutralized. From this it appears that the acid is mostly, if not wholly, organic.

It has been, thus far, impossible to discover what acid or acids were united to the albumin. Neutralization of the albumin suspended in fifty per cent. alcohol resulted in the formation of a gummy mass difficult to filter and wash, and from which none of the products of neutralization could be separated. Neutralization of a solution of ten grams of the albumin and dialysis in distilled water, failed to give enough salts in the diffusate to shed light on the nature of the acid. Neutralization with baryta of a

[1] Sabanejeff : *Chem. Centrbl.* (*1891*), 10, found the molecular weight of purified egg albumin by determining the lowering of the freezing-point to be 15,000.

solution of two grams of the albumin gave a very slight precipitate, which after standing some days, was filtered out, washed and ignited, but only four milligrams of mineral matter were obtained.

The preparations showed no excess of sulphur over that usually found in coagulated and thoroughly washed albumin prepared without the use of sulphuric acid or sulphates. Determination of total phosphorus showed A.1 and H.1 to contain 0.38 and 0.40 per cent. phosphorus pentoxide respectively. These preparations contained 0.87 and 0.69 per cent. of ash which was almost wholly insoluble in water and appeared to consist chiefly of calcium phosphate. The total phosphorus in these preparations was equal to 0.59 and 0.64 per cent. of tricalcium phosphate respectively.

Towards lacmoid these preparations reacted alkaline, about one cc. of decinormal acid being required to neutralize the solution of one gram, and three cc. to give an acid reaction. When one gram was treated with decinormal hydrochloric acid, no evidence of free acid was shown with tropæolin, until eight or nine cc. were added.

When pure water solutions containing two and five-tenths per cent. of my albumin preparations were heated they all became turbid at 58°–59° and separated a minute quantity of flocks at 59°–60°. On gradually raising the temperature the coagulum slowly increased until at 70° much of the dissolved albumin had coagulated. The solutions heated for some time at 74° and filtered still contained a little proteid which even on heating at 99° did not separate until some salt was added. No break in this gradual coagulation of the albumin was detected, the solutions when filtered after partial coagulation yielding a coagulum on again heating up to the temperature to which they had been developed at previously heated.

When solutions of pure ten per cent. sodium chloride brine containing two and one-half per cent. of each of these preparations except A.3, H.3 and A.4 were slowly heated, turbidity developed at 56°–59° and flocks at 56°–60°.

Only a trace of coagulum was obtained, however, below 64°, and the solutions filtered from this remained perfectly clear until heated to nearly or quite 70°, when the albumin began to coagulate. It was, however, found necessary to heat the solution to nearly 84° before most of it was separated.

The three preparations A.3, H.3, and A.4, behaved as just described, except that below 64° each yielded a relatively considerable coagulum. These preparations, it is to be noted, are final fractions obtained in small quantity and it seems probable that this coagulum obtained at 60°–64° is due to the presence of a different substance from that constituting the chief part of the other fractions. This is the more probable as A.3 and A.4 also showed a difference in specific rotation, as well as in composition.

The degree of acidity was found to have much influence on the coagulation of the albumin. Exact neutralization to phenolphthalein, as might be expected, entirely prevented coagulation, even on boiling. When the acid of the albumin was neutralized so that the acidity was equal to one and two-tenths cc. of decinormal solution per gram of albumin, a solution containing two and five-tenths per cent. of the proteid became slightly opalescent on heating to 72° and remained otherwise unchanged, even after heating for a long time in a boiling water-bath. If, however, the acidity was but one-tenth cc. greater, that is, equal to one and three-tenths cc. per gram of albumin, the solution became turbid at 70°, and very opaque after heating in the water-bath at 99°. The difference between the two solutions was marked and it is evident that the additional one-tenth cc. had caused a change in the condition of the albumin. An acidity of 1.33 cc. per gram is almost exactly equal to two molecules of acid per molecule of albumin, assuming the latter to have a molecular weight of 15,000. From this it would seem to be necessary to add three molecules of acid to one of albumin, in order to form the coagulable substance.

The specific rotation of these preparations was approximately determined by means of a Schmidt and Haensch polarimeter using a 200 mm. tube. The readings on the sugar scale were converted into degrees of circular polarization by multiplying by 0.346. The formula used in calculating the results was

$$(a)_D = \frac{a \times 100}{p \times d \times l} \quad \text{where}$$

a = observed rotation,
p = per cent. of albumin in the solution,
d = density of the solution,
l = length of tube in decimeters.

The results obtained were as follows:

Preparation.	Per cent. of dissolved albumin.	Solvent.	Rotation.		Average.	
A.1	$\left\{\begin{array}{l}5.861 \\ 6.670\end{array}\right.$	Water "	$-29° \ 48'$ $-28° \ 46'$	$\left.\right\}$	$-29°$	$17'$
A.2	3.422	"			$-29°$	$23'$
A.3	3.273	"			$-33°$	$3'$
A.4	3.404	"			$-41°$	$45'$
H.1	$\left\{\begin{array}{l}3.425 \\ 3.237 \\ 6.478\end{array}\right.$	10 per cent. NaCl Water "	$-29° \ 0'$ $-28° \ 33'$ $-28° \ 1'$	$\left.\right\}$	$-28°$	$35'$
H.2	1.699	"			$-28°$	$14'$
H.3	3.205	"			$-39°$	31

As the results obtained on A.1, A.2, H.1, and H.2, agree closely and as these preparations represent very different proportions of the total albumin of the egg white, it seems probable that we have in these fractions but one substance.

Bondzynski and Zoja, working with solutions containing ammonium sulphate, obtained similar but somewhat lower figures for the specific rotation of their least soluble fractions; namely, 25° 8′ and 26° 2′, duplicate determinations on the same fraction. Two other fractions gave them 34° 18′ and 42° 54′, figures agreeing fairly with those obtained by me for my more soluble fractions. They determined the albumin in the polarized solution by coagulation, a process which does not admit of so exact a determination of the dissolved albumin as that employed by me, which consisted simply in evaporating the pure water solution to dryness, drying to constant weight at 110° and deducting ash. A slight error in determining the dissolved albumin causes a considerable error in the specific rotation.

The effect of acid and alkali on the rotation of the albumin solutions is shown by the following results, obtained by dissolving one gram of A.2, in twenty-five cc. of water and treating with the given quantities of acid or of alkali :

1 gram A.2 + nothing		$-29° \ 17'$
+ 0.8 cc.	N/10 HCl	$-29° \ 5'$
+ 8.0 cc.	"	$-33° \ 46'$
+ 1.4 cc.	N/10 KOH	$-28° \ 45'$
+ 2.7 cc.	"	$-30° \ 20'$
+ 4.2 cc.	"	$-32° \ 30'$

It is to be noted that by eight cc. of the acid and by four and two-tenths cc. of the alkali a rotation was produced about ten

per cent. higher than with the smaller quantities of acid or alkali. This increase may well be due to a local overreaction taking place on mixing the acid and alkali with the proteid solution, it having been demonstrated that large proportions of acids and alkalies yield products of high specific rotation.

Panormoff[1] has studied the specific rotation of fractionally precipitated crystallized egg albumin and concludes that there are two albumins present in egg white, one with a specific rotation of —23.6° and the other —46.2°. The albumin with the lower rotations he obtains from the so-called egg globulin precipitated by adding an equal volume of saturated ammonium sulphate solution to the egg white. This he succeeded in crystallizing and, so prepared, finds it to have the properties and composition of albumin. He considers, therefore, the egg globulin to be a compound of egg albumin with some unknown substance.

As the egg white is alkaline to litmus and ammonia is set free on adding to it a saturated solution of ammonium sulphate, it is not surprising that a product should be produced of different solubility from that of the albumins which we have been considering.

Panormoff converted his crystallized albumin into a chloride by dialysis against two-tenths per cent. hydrochloric acid. He analyzed the product obtained and it is interesting to note that, if calculated free from hydrochloric acid, the figures for the albumin are in exceedingly close agreement with the average of the best analyses of albumin. Furthermore, the proportion of hydrochloric acid in the compound is exactly the same as that which I found with tropæolin to be fixed by the albumin; that is, I found that one gram of albumin united with eight cc. of decinormal acid or 0.0292 hydrochloric acid to form a compound showing no free acid with tropæolin, while Panormoff's chloride contained 2.92 per cent. or exactly the same quantity.

In regard to the composition of egg albumin, confusion has recently been caused by Hofmeister, who states[2] that he has found in repeatedly crystallized egg albumin 1.01 and 1.18 per cent. of sulphur and that Dr. F. N. Schulz, in his laboratory, has obtained 1.24 and 1.27 per cent. He consequently calls in ques-

[1] Ref. in *Chem. Centrbl.* (*1898*), II, 358 and 487.
[2] *Ztschr. physiol. Chem.*, 24, 166.

tion the purity of the samples of crystallized albumin, analyzed with great care by Bondzynski and Zoja. As Hofmeister's figures for carbon are higher and for nitrogen lower than those of Bondzynski and Zoja, as well as of other investigators who have analyzed *amorphous* egg albumin, the whole question of the composition of this substance is again thrown into confusion.

Having at hand a sample of egg albumin, which had been three times recrystallized in the manner described by Hofmeister as necessary for its purification, and obtained in the same proportion from the egg white as stated by him to be the usual yield after thorough purification, and which had been coagulated with alcohol and thoroughly washed until all the ammonium sulphate had been removed, I analyzed it, dried at 110°, with the result given under No. 1.

Analyses of the seven fractionally crystallized preparations A.1-4, and H.1-3, were made after drying them to constant weight at 110°.

	No. 1.	H.1.	H.2.	H.3.
Carbon	52.18	52.85	52.33	51.72
Hydrogen	6.91	6.92	6.90	6.90
Nitrogen	15.67	15.66	15.77	15.26
Sulphur	1.70	1.572	1.644	1.958
Oxygen	23.54	22.998	23.356	24.162
	100.00	100.00	100.00	100.000
Ash	0.56	0.69	0.67	0.59
Total phosphorus pentoxide	....	0.40	0.21	trace

	A.1.	A.2.	A.3.	A.4.
Carbon	52.60	52.61	52.33	51.44
Hydrogen	7.02	6.94	6.93	6.88
Nitrogen	15.54	15.76	15.40	15.20
Sulphur	1.610	1.612	1.778	1.912
Oxygen	23.230	23.078	23.562	24.568
	100.000	100.000	100.000	100.000
Ash	0.87	0.65	0.67	0.40
Total phosphorus pentoxide	0.37	0.28	trace	trace

There can no longer be question about the amount of sulphur in albumin being greater than that stated by Hofmeister. My sulphur determinations were made with extreme care, fusing more than a gram of the substance over an alcohol lamp with

pure sodium hydrate and peroxide in a nickel crucible,[1] dissolving the fusion in an excess of hydrochloric acid, neutralizing most of the excess of acid and precipitating with barium chloride from a boiling solution of at least 800 cc. volume. Blank determinations showed no trace of sulphur in the reagents and also that none was absorbed during the fusion over the alcohol lamp. These results agree with those obtained by Bondzynski and Zoja, though the difference in composition between their extreme fractions was not quite so great as found for my preparations.

The composition, rotation, heat-coagulation points and reactions of the crystallized egg albumin obtained by aid of hydrochloric or acetic acids show this to be the same substance as that which has in the past been regarded as egg albumin.

My results, those of Bondzynski and Zoja, and of Panormoff, make it plain that there are two protein substances in the egg white, which are commonly obtained admixed when preparing egg albumin by the usual processes. Whether the extremes of my fractional precipitations of these two albumins consist wholly or even largely of each one of these bodies requires further investigation of large quantities of egg white. This work we now have well under way.

Moerner[2] has described ovomucoid as identical with Neumeister's pseudopeptone,[3] and states that it constitutes about one-eighth of the organic substance of the egg white. As this substance is described as largely, though not wholly, precipitated by two-thirds saturation of its solution with ammonium sulphate, it ought, if present as such in the egg white, to be found among the more soluble fractions thrown down by successive additions of ammonium sulphate. It is intended to direct especial attention to the isolation of this substance and to determine if possible in how far it may be admixed with the albumins.

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[1] I have found many times when using a nickel crucible that, on dissolving the fusion, there was a black substance present (this looks and behaves like nickel sulphide, but it seems hardly possible that nickel sulphide could escape oxidation), which, when filtered out and oxidized, was found to contain sulphur. This black substance should be dissolved by the chlorine liberated from the hydrochloric acid by the peroxide of hydrogen, otherwise too low results will be obtained.

[2] *Ztschr. physiol. Chem.*, **18**, 525.

[3] *Ztschr. Biologie*, **9**, 360.

ON SOME DEFINITE COMPOUNDS OF PROTEIN-BODIES.

By Thomas B. Osborne.

PROTEIN-BODIES, as hitherto prepared in a state fit for the study of their composition and properties, are commonly considered to be, for the most part, distinct organic molecules, not united to either acids or bases.

Although protein-bodies are known to combine or react with acids, bases and halogens, scarcely any of their compounds or derivatives have been as yet described of constant or definite composition, except in cases where the original substance has been profoundly modified or broken up.

The object of this notice is to state briefly some results of an investigation which leads to the conclusion that protein-bodies, as hitherto prepared, are, in fact, definite chemical compounds of protein-substance with common mineral acids, or contain such compounds in admixture.

A large number of the purest protein-preparations that it has hitherto been possible to make in this laboratory, including egg albumin several times recrystallized, edestin, legumin, excelsin, amandin, corylin, phaseolin, gliadin, hordein and zein,[1] are, without exception, acid to phenolphthalein, slightly acid or neutral to litmus and decidely alkaline to lacmoid.

To render gram portions of the above-named substances neutral to litmus has required in some cases not any, in others from one-tenth cc. to one cc., and in a very few instances a little more than one cc. of decinormal alkali solution. To make the same gram portions neutral to phenolphthalein, a further quantity of about one cc. of decinormal alkali has been required, except for legumin, which took up about two cc.

By help of lacmoid and other indicators, it can be shown that these protein-bodies are able to combine with additional quantities of acids.

In case of edestin preparations,[2] that had been deposited from

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[1] See papers by the author and his associates in *Am. Chem. J.*, **13, 14** and **15.** This Journal, **16, 17, 18, 19,** and **20.** Also Griessmayer, Die Protiede, etc., Heidelberg, 1897.

[2] Edestin is one of several crystallized substances which are frequently termed plant-vitellin. It was first prepared by Barbieri from squash seeds, and was obtained in distinct crystals by Grübler. It was afterwards extracted from seeds of hemp, castor bean and sunflower, by Ritthausen. (*J. prakt. Chem.*, (2) **18,** 102; **23,** 97 and 481.) The author and his associates have identified it in the seeds of flax, cotton, wheat, rye, barley, and maize. See also *Am. Chem. J.*, **14,** 671 ; this Journal, **18,** 609.

salt solutions, I have undertaken to determine what acids are present which thus react with an alkali.

When such an edestin preparation is suspended in water and made neutral to phenolphthalein, edestin itself, pure and simple, remains undissolved, while the added alkali carries into solution its equivalent of the acid or acids which had been united to the edestin.

What acids are thus removed from edestin depends upon the conditions of its preparation, that acid being predominant which was most abundant as a mineral salt in the solution from which the edestin last separated.

Accordingly, edestin that has been precipitated from sodium chloride brines carries with it hydrochloric acid chiefly, but, when thrown down from ammonium sulphate solutions, it is united to sulphuric acid. It appears to be also in small part combined to an organic acid, as yet unidentified, whose alkali salt yields carbonate when ignited.

The smallest quantities of alkali carbonate and, therefore, it is to be inferred of organic acid, have come from those preparations which have been repeatedly deposited out of sodium chloride brine.

The solutions hitherto obtained on thus neutralizing edestin preparations with alkali, have invariably contained a very little organic matter which when strongly heated gives out a peculiar characteristic odor and yields alkaline vapors.

Property of Edestin.—Before giving further account of edestin compounds, it is best to state explicitly some of the characters of edestin itself.

As before mentioned, when preparations which contain edestin chemically united to acids are suspended in a little water and made exactly neutral to phenolphthalein by addition of dilute solution of potassium hydroxide, the edestin remains undissolved, and after washing with pure water is, so far as we have been able to discover, entirely free from the acids that were combined with it.

Thus isolated edestin is insoluble in pure water, but dissolves readily in decinormal alkali and also in decinormal hydrochloric acid. Of the alkali seven-tenths cc. and of the acid one and

four-tenths cc. are required to effect the solution of one gram of water-free edestin.

Pure edestin dissolves freely in a ten per cent. brine of pure sodium chloride. This solution, freshly prepared, is neutral to phenolphthalein, but alkaline to litmus and strongly alkaline to lacmoid. When this solution is heated to 99° in a boiling water-bath, it is very slowly and imperfectly coagulated.

Solution of edestin in ten per cent. brine, when saturated with sodium chloride, is precipitated slightly; when saturated with magnesium sulphate, it is precipitated more largely, and on saturating with sodium sulphate at 34°, the edestin is thrown down completely.

EDESTIN HYDROCHLORATES.

Monohydrochlorate.—If pure edestin, neutral to phenolphthalein, be dissolved in ten per cent. sodium chloride brine and gradually mixed with an equal volume of the same brine containing one cc. of decinormal hydrochloric acid for each gram of edestin, a nearly or quite clear solution is obtained, which, when dialyzed, yields a wholly crystalline deposit. On washing with water a part of this deposit dissolves after the salts have been removed, and a part remains undissolved being wholly insoluble in water. This latter substance is edestin monohydrochlorate.

When dissolved in brine, one gram of this salt is neutralized to phenolphthalein by seven-tenths cc. of decinormal alkali solution. Assuming that edestin has a molecular weight of about 14,300,[1] this body, insoluble in water, consists of one

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[1] The simplest formula for edestin (containing two atoms of sulphur) which can be calculated from the average of a large number of closely agreeing analyses (carbon, 51.55; hydrogen, 6.92; nitrogen, 18.67; sulphur, 0.90; oxygen, 21.96) gives a molecular weight of 7,138, twice which is 14,276, the formula being, carbon, 614; hydrogen, 988; nitrogen, 190; sulphur, 4; oxygen, 196.

Calculation of similar formulas for plant globulins containing but four-tenths per cent. of sulphur shows that these substances, if there are two atoms of sulphur in the molecule, must have a molecular weight of not less than 14,500. The same is true for globin from oxyhaemoglobin recently analyzed by Schultz. Closely agreeing molecular weights for the more carefully analyzed protein-bodies can be calculated from their analyses by multiplying the simplest formula containing one atom of sulphur by such a factor that each formula shall contain two or more atoms of sulphur and have a molecular weight nearest to 15,000. For twenty-seven distinct protein-bodies of vegetable and animal origin formulas strikingly similar to that above given for edestin are so obtained, and also molecular weights, nearly all of which are very nearly 15,000, the extremes being 14,068 and 16,074. Those protein substances known to be compound bodies, like oxyhaemoglobin and casein, give higher molecular weights. The number of sulphur atoms in these formulas ranges from two to ten. One gram of substance having a molecular weight of 15,000 would require for a complete molecular reaction 0.66 cc. of a decinormal solution.

molecule of edestin combined with one molecule of hydrochloric acid.

When pure edestin is dissolved in ten per cent. neutral sodium chloride brine and the solution, which is neutral to phenolphthalein, is dialyzed, imperfectly developed crystals are deposited that, when dissolved in neutral brine, yield a solution having an acidity nearly or quite equal to that of edestin monohydrochlorate.

Edestin monohydrochlorate is wholly insoluble in water, but dissolves in ten per cent. sodium chloride brine to a solution from which it is readily thrown down by adding water. On warming the thus diluted brine, the precipitate dissolves and reappears on cooling in octahedral crystals.

A solution containing five per cent. of edestin monohydrochlorate and ten per cent. of sodium chloride becomes turbid when heated to 95°, and a flocculent coagulum separates slowly on continued heating at 99°.

Edestin Bihydrochlorate.—When pure edestin is treated with insufficient dilute hydrochloric acid to dissolve it all, the part dissolved consists of bihydrochlorate of edestin. To neutralize to phenolphthalein one gram of edestin thus dissolved, one and one-fourth cc. of decinormal alkali are required, and in the solution from which edestin is thereby precipitated, alkali chloride is formed very nearly equivalent to the alkali added.

Edestin bihydrochlorate is soluble in pure water, its solution therein being, however, precipitated by very small quantities of alkali salts. Although quite insoluble in one or two per cent. sodium chloride brine, edestin bihydrochlorate freely dissolves in ten per cent. salt solution.

From ten per cent. sodium chloride brine the bihydrochlorate separates on dialysis in octahedral crystals. By diluting its solution in ten per cent. brine a precipitate is formed, which dissolves on warming the diluted brine. On cooling, this solution deposits the substance in very perfect crystals.

The ten per cent. sodium chloride solution of edestin bihydrochlorate, like the similar solutions of the monohydrochlorate and of edestin, gives, when saturated with sodium chloride, a very slight precipitate; when saturated with magnesium sul-

phate, somewhat more, and saturated at 34° with sodium sulphate is completely precipitated.

A solution containing ten per cent. of sodium chloride and ten per cent. of edestin bihydrochlorate gives a slight precipitate when mixed with one-half its volume of water, and a rapidly increasing precipitate on continued dilution.

A solution containing ten per cent. of sodium chloride and five per cent. edestin bihydrochlorate gives a slight precipitate with an equal volume of water. When heated in a double water-bath, ten per cent. salt solution containing five per cent. of edestin bihydrochlorate becomes turbid at 90° and at 91° flocks separate, which gradually increase in quantity on heating at 99°. Edestin bihydrochlorate dissolved in water or salt solution reacts acid to phenolphthalein and litmus, but is strongly alkaline to lacmoid.

When the solution of edestin bihydrochlorate in water is made neutral to phenolphthalein, by addition of alkali, the edestin separates out completely and is then almost entirely soluble in ten per cent. brine.

From the water solution of edestin bihydrochlorate the edestin is completely thrown down by small quantities of soluble salts; but this precipitate is not wholly redissolved by ten per cent. brine, a relatively small portion remaining insoluble, which is more acid than edestin bihydrochlorate while the substance redissolved is less acid and shows the properties of a mixture of the mono- and bihydrochlorate.

OTHER ACID SALTS OR DERIVATIVES OF EDESTIN.

1. The substance insoluble in ten per cent. solution of sodium chloride, last mentioned in the preceding paragraph, is or contains a third more acid compound or derivative of edestin, which on neutralization yields a product wholly different from edestin, which is now under investigation. Its study is expected to throw light on the nature of "acid albumin" and of Weyl's "albuminate."

2. All edestin preparations, obtained from sodium chloride extracts of hemp-seed by dialysis or by cooling, when dissolved in a minimum of hydrochloric acid, react so strongly alkaline

with lacmoid[1] that a total of from two and five-tenths to three cc. of decinormal acid are required to neutralize to lacmoid the solution of one gram of edestin, and to obtain an acid reaction with this indicator a total of about eleven cc. of acid per gram are necessary.

3. On treating several gram portions of edestin with uniformly increasing quantities of decinormal hydrochloric acid and testing for free acid with mixed potassium nitrite, iodide and starch paste, a very marked difference was seen in the intensity of the reaction, between six and five-tenths cc. of decinormal acid per gram or less, and seven cc. or more, strongly indicating a firmer binding of the smaller quantity of acid.

4. With tropæolin no reaction for free hydrochloric acid could be obtained until thirteen cc. of decinormal acid had been added, a quantity just twice that found in testing for free acid with potassium nitrite.

Closely agreeing figures are given by this indicator, and different preparations of the same protein body have given accordant results; thus, three different samples of edestin reacted with 12.9 cc., 12.5 cc, and 12.7 cc.

Many other protein preparations thus tested have shown that from nine to thirteen cc. of acid are bound by one gram of substance. Excelsin fixed 12.4 cc.; legumin from three different seeds fixed 12.5 cc., 12.9 cc., and 13.4 cc.; amandin took up 10.3 cc. and crystallized egg albumin 9 cc.

Whether the results of the interaction of edestin with these larger quantities of hydrochloric acid are simply edestin salts, or products of its decomposition or alteration, is as yet undetermined.

Edestin forms soluble compounds with nitric and acetic acid in the same molecular proportions as with hydrochloric acid.

When former edestin preparations (separated from salt solution by dialysis), which yield on neutralization chlorides, sulphates, in some cases traces of phosphates, and always more or less organic matter, are suspended in water and treated with measured amounts of hydrochloric acid (not in excess), they dissolve in proportion to the quantity of acid added, provided the amounts of water-soluble substance (bi-acid edestin) orig-

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[1] Blood, milk and other animal fluids, as well as saline extracts of seeds, react strongly alkaline with lacmoid.   This reaction, though doubtless due to some extent to alkaline phosphates, is unquestionably chiefly caused by the protein constituents of the fluid.

inally contained in the preparations be deducted from the total quantities dissolved. Thus, several series of determinations of the solubility of edestin were made by suspending gram portions in water enough to make a final volume of twenty cc. and adding successively increasing quantities of centinormal hydrochloric acid. After frequently shaking during several hours, the solutions were allowed to settle, filtered clear, the acidity to phenolphthalein determined, the solutions evaporated, the residues dried at 110° and weighed.

It was found that the amount of edestin thus dissolved increases quite uniformly with increased quantity of acid, and that a little over 0.11 gram of the substance is carried into solution by each additional cc. of centinormal hydrochloric acid. The acidity of the soluble body thus produced is very nearly that of a compound of edestin with two molecules of monobasic acid.

Those preparations which yield relatively much alkali sulphate on neutralization are less soluble in hydrochloric acid than the others, and the water-soluble edestin compounds resulting are relatively more acid, since pure edestin requires for solution more sulphuric than hydrochloric acid, and the soluble edestin sulphates are much more acid than the soluble bihydrochlorate. All the preparations of edestin whose solubility in hydrochloric acid we have determined yield more or less alkali sulphate on neutralization. To this fact we attribute the slightly less degree of solubility in hydrochloric acid found than that calculated for a compound of two molecules of acid with one of edestin (molecular weight assumed to be 14,300), and also the correspondingly slightly greater acidity of the dissolved substance.

Edestin Sulphates.—Determinations of the solubility in sulphuric acid of edestin give tolerably uniform results for one and the same preparation, but differ for different preparations. With increasing quantities of sulphuric acid the degree of acidity of the soluble products increases uniformly up to many times that of the bihydrochlorate. This behavior with sulphuric acid is due to the fact that the preparations tested were largely hydrochlorates. Definite results cannot be had until preparations free from acids other than sulphuric have been made and tested, which work we now have in hand.

What has been said of sulphuric acid applies, though to a less degree, to phosphoric acid, a centinormal solution of which dissolves about one third as much edestin as a like solution of hydrochloric acid. In other words, tribasic phosphoric acid in dissolving edestin appears to act as a monobasic acid.

A study of the relations to bases and acids exhibited by many other protein substances is in progress, the results of which will be published soon. So far as yet discovered, all other protein preparations are compounds of a similar character to those of edestin. Although much evidence to this effect has been obtained, details are reserved until the entire accuracy of the results is confirmed and the study extended so that it may be made more complete.

It is unnecessary to point out the importance of the fact that what have been heretofore regarded as "native" protein substances are, in fact, protein bodies combined to acids, so that preparations as usually obtained have been mixtures of the simpler salts of these bodies. In this fact we will doubtless find an explanation of many of the minor differences noted between protein preparations which appear to be otherwise identical. Thus, the difference between the albumins of the eggs of different kinds of birds, between the haemoglobins of the blood and the caseins of the milk of different animals may well be thus explained.

Courrant's studies of the proportion of alkali and acid neutralized by casein makes it seem highly probable that nucleoalbumins will prove to be phosphoric acid compounds similar to those described in this paper, but containing several molecules of acid.

Fuerth's account of the protein bodies of the muscle plasma indicates that the confusion which has existed in relation to these substances is probably due to the formation during extraction and separation of a series of increasingly acid compounds of one or more protein bodies. The sensitiveness of many enzymes to alterations in reaction is not improbably connected with the formation of definite acid compounds.

The unexplained, apparently spontaneous, alteration of protein substances is in many cases certainly due to the formation of acid compounds.

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THE THEORY OF THE FORMATION OF NICKEL SULPHIDE.

BY J. LIVINGSTON R. MORGAN AND A. H. GOTTHELF.

NICKEL sulphide is precipitated from alkaline solutions by hydrogen sulphide gas, and when once formed is insoluble in dilute acids. Notwithstanding this insolubility, however, the precipitate is not formed when the gas is passed through a solution containing this strength of acid. By following out the general laws as to the formation of the metallic sulphides it is possible to explain this anomalous behavior in quite a simple way, and the object of this paper is to present and prove this theory as applied to nickel sulphide. Since cobalt sulphide behaves in the same manner, it is not necessary to go into details regarding it. As yet it is not known whether ions of sulphur exist in the free state, $\overset{-}{S}\overset{-}{}$, or are always combined with hydrogen in the form $\overset{-}{HS}$. *In this paper we shall consider that free ions of sulphur, $\overset{-}{S}\overset{-}{}$, do exist, but it is only for the sake of simplicity.* If hydrogen sulphide ionizes according to the scheme,

$$H_2S = \overset{+}{H} + \overset{-}{HS},$$
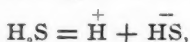
then all sulphides will do the same ; *viz.*,

$$MS + H_2O = \overset{+}{M} + \overset{-}{HS} + \overset{-}{OH},$$
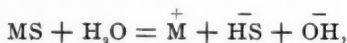
so that the relation of the concentrations of $\overset{-}{HS}$ ions in the two sulphides will be the same as would that of the $\overset{-}{S}\overset{-}{}$ ions, if they were formed. Since the sulphide is formed, it is simpler to consider $\overset{-}{S}\overset{-}{}$ ions to be present, for then the sulphide is formed directly. When $\overset{-}{HS}$ ions are present the reaction would be

$$\overset{++}{M} + 2\overset{-}{Cl} + 2\overset{-}{HS} + 2\overset{+}{H} = MS + H_2S + 2\overset{+}{H} + 2\overset{-}{Cl},$$
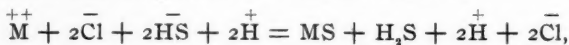
the result being the same, but reached in a more complicated

way.   It is to be remembered then that, although we speak of $\overset{-}{S}$ ions, it is not necessary that they exist, for all conclusions will still hold with $\overset{-}{HS}$ ions, providing only that the metallic sulphides dissociate in the same way as hydrogen sulphide does, a fact which is well known.

All substances are soluble to a certain extent, the term insoluble being only a relative one.   Nickel sulphide in water, then, goes into solution to a certain extent, as undissociated nickel sulphide and as ions of $\overset{++}{Ni}$ and $\overset{-}{S}\overset{-}{}$.   The equation of equilibrium which regulates the amount of each of these products is

$$\overset{++}{Ni} \times \overset{-}{S}\overset{-}{} = K_0 \times NiS ;$$
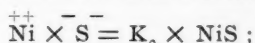
i. e., the product of the concentrations of the ions is equal to the concentration of the undissociated portion multiplied by the ionization constant, the concentrations being expressed in gram-molecules per liter.   According to Nernst in a saturated solution, the undissociated portion always remains constant.   If by any means, then, the dissociation is driven back, a certain amount of undissociated nickel sulphide will be formed, which will separate out as a solid, since the solution is already saturated with it.   In the equation of equilibrium we have, then, two constant terms upon the right side, hence the left side must also remain constant ; *i. e.*,

$$\overset{++}{Ni} \times \overset{-}{S}\overset{-}{} = K.$$
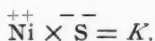
This term K is called the *solubility product* of the nickel sulphide.   The meaning of K in words is as follows: If $\overset{++}{Ni}$ and $\overset{-}{S}\overset{-}{}$ ions are present together in a liquid, no undissociated nickel sulphide will be formed until this product is exceeded, in which case enough undissociated nickel sulphide will be formed to cause the product of the concentrations of the ions still free to just reach this value, K.   The undissociated NiS will first saturate the solution, the remainder separating out as a solid.   The amount of $\overset{++}{Ni}$ ions will be the smaller the greater the amount of $\overset{-}{S}\overset{-}{}$ ions, for the product must remain constant.   If in a solution we have a small number of metal ions, it is necessary to

have an excess of $\overline{S}$ ions in order that the solubility product may be exceeded, and undissociated sulphide formed. The smaller the solubility product the smaller will be the number of $\overline{S}$ ions necessary for precipitation. Upon the size of the solubility product depends, then, the behavior of the salt solutions of a metal toward hydrogen sulphide gas. If the product is small enough to be exceeded by the aid of the ions of $\overline{S}$ contained in a solution of hydrogen sulphide gas, the metal will belong to one of the higher analytical groups. If the product is large, then it will only be reached by an alkaline sulphide, for that contains ' more ions of $\overline{S}$ than a saturated solution of hydrogen sulphide gas. We can divide the metals, then, into two groups, those which have products which can be exceeded by the $\overline{S}$ ions in hydrogen sulphide solution, and those whose products can only be exceeded by a greater number of $\overline{S}$ ions. Metals of the former class will be precipitated by hydrogen sulphide in neutral or acid solutions, those of the latter only in alkaline solutions. Some metals are partly precipitated in neutral solutions. This is due to the fact that the solubility product is at first exceeded by the simple hydrogen sulphide solution. Later, since acid is formed by the reaction, the $\overset{+}{H}$ ions increase and cause the $\overline{S}$ ions of the hydrogen sulphide to decrease to such an extent that the product is no longer exceeded. The amount of the sulphide precipitated from the neutral salt depends, then, upon the strength of the acid formed, for the greater its dissociation constant the more the dissociation of the hydrogen sulphide will be affected. Since nickel, cobalt, and zinc are precipitated by hydrogen sulphide in presence of weak acids, their sulphides partake of the characteristics of the higher as well as of the lower group of metals. The solubility products must therefore be smaller than those of the others of the iron group and greater than those of the copper group. We see, then, that the division between the two general groups is not sharply defined, and so we should expect to find an anomalous action of some kind in connection with the metals of the middle group. In the case with zinc this is not observed because it partakes more

of the characteristics of the upper than the lower group, but with nickel and cobalt it is marked. When nickel sulphide is brought in contact with strong hydrochloric acid, hydrogen sulphide gas and nickel chloride are formed. Hydrogen sulphide, however, can only be formed when the product of the concentration of $\overset{+}{H}$ ions multiplied by that of the $\overset{-}{S}$ ($\overset{-}{H}\overset{-}{S}$) ions exceeds the solubility product. Then the gas formed saturates the solution and is given off in the gaseous state. A sulphide which in a water solution has a larger concentration of $\overset{-}{S}\overset{-}{}$ ions than exists in a saturated solution of pure hydrogen sulphide, must be soluble in acid, for the product $\overset{+}{H} \times \overset{-}{S}\overset{-}{}$ ($\overset{-}{H}\overset{-}{S}$) will be greater than the solubility product of hydrogen sulphide. Such a sulphide could also only be formed in an alkaline solution; *i. e.*, one in which there is a greater number of $\overset{-}{S}\overset{-}{}$ ions than in hydrogen sulphide. The process of solution is quite simple, ions of $\overset{+}{H}$ and $\overset{-}{S}\overset{-}{}$ ($\overset{-}{H}\overset{-}{S}$) are together in large numbers and so unite to form undissociated hydrogen sulphide. This leaves the solution unsaturated with the ions, hence more of the sulphide dissolves and dissociates, the process continuing until all the sulphide is dissolved or all the acid used up.

A sulphide which contains a smaller number of $\overset{-}{S}\overset{-}{}$ ($\overset{-}{H}\overset{-}{S}$) ions in a saturated solution than exists in a solution of hydrogen sulphide, will be insoluble in acid, since the solubility product of hydrogen sulphide cannot be exceeded, and the salts will be precipitated by hydrogen sulphide even in the presence of acid.

The smaller the solubility-product of the sulphide the more rapidly will the sulphide be formed by hydrogen sulphide. The greater the solubility-product of a sulphide the more rapidly it will dissolve in acid. Nickel sulphide has a solubility-product which lies between these two extremes, and must contain in a saturated solution a slightly smaller concentration of $\overset{-}{S}\overset{-}{}$ ($\overset{-}{H}\overset{-}{S}$) ions than hydrogen sulphide (otherwise nickel sulphide would not be formed in presence of acid). The difference in concentration of $\overset{-}{S}\overset{-}{}$ ions must be small, for a little acid prevents

the precipitation by decreasing the difference.   The anomalous
behavior of the sulphide is due to this small difference.   To cause
the sulphide to dissolve it is necessary to have $\overset{+}{H}$ ions present
to such an extent that the $\overset{-}{S}$ ($\overset{-}{H}\overset{-}{S}$) ions in the hydrogen sul-
phide formed may be smaller in number than those of the sul-
phide.   If the acid is of such a strength that hydrogen sulphide
in it would have the same, or nearly the same, concentration of
$\overset{-}{S}$ ions as the sulphide, the speed of solution will be almost
infinitely slow ; *i. e.*, practically no solution will take place dur-
ing any short period of time.   The sulphide will then remain in
its original state.   As the amount of acid is increased, its $\overset{+}{H}$ ions
decrease the number of $\overset{-}{S}$ ($\overset{-}{H}\overset{-}{S}$) ions which are necessary to
exceed the solubility-product of the hydrogen sulphide gas, and
finally it is formed.   The velocity of the change will increase
slowly with the concentration of acid, but no sharp distinction
can be made.

If we attempt to precipitate nickel sulphide from a nickel salt
in the presence of acid of such strength that hydrogen sulphide
has nearly the same concentration of $\overset{-}{S}$ ions as the nickel sulphide
would have if it were formed, no sulphide will be formed for the
velocity of formation will be almost infinitely slow.

In short, if two substances have the same concentration of one
kind of ion, the one will not be transformed into the other.   If
there is but a slight difference between the concentrations, the
reaction will take place, but so slowly that it will not be observed
until the concentration difference is marked.   The substance which
is present will always remain unaltered until the difference
becomes great enough to cause a certain speed of reaction.   This
is the proposed theory for the explanation of the behavior of
nickel and cobalt sulphides.   In a few words it may be summed
up as follows :

The concentration of $\overset{-}{S}$ ($\overset{-}{H}\overset{-}{S}$) ions in a saturated solution of
nickel sulphide or cobalt sulphide is so little less than that in a
saturated solution of hydrogen sulphide gas, that addition of a
small amount of acid causes the latter to decrease to nearly the

value of the former, so that the substance which is already present (hydrogen sulphide or nickel sulphide) remains unchanged, owing to the slight velocity of the change which is proportional to the difference in concentration of the two with respect to the $\overline{S}$ ($\overline{HS}$) ions.[1]

As to the proof for this, the fact that the sulphide is formed in the presence of a large amount of acetic acid and also in that of a small amount of hydrochloric acid shows that the formation is simply a question of the concentration of sulphur ions. Neutral solutions, as the dichloracetate, allow a certain amount of precipitate to be formed ; *i. e.*, until the concentration of the $\overset{+}{H}$ ions of the acid formed causes the two concentrations of $\overline{S}$ ($\overline{HS}$) ions to become equalized. The clearest proof would be to compare the solubility-products of the nickel sulphide and hydrogen sulphide,[2] but, unfortunately, this is impossible, for neither is known. It seems, however, hardly necessary to go to such an extent as this to prove the correctness of the theory, for it is thought that the results which have been given already and those that follow are conclusive, although such a final comparison would be of interest.

The results of the analyses given below show quantitatively just what effect an acid has upon the amount of nickel sulphide formed. The amount precipitated in nickel dichloracetate is too small, for the latter was found afterward to contain free acid, the amount of which could not be determined. Nickel acetate is almost completely precipitated in a neutral solution, which was partly prevented by the addition of varying amounts of hydrochloric acid, and the amount of nickel sulphide determined.

[1] Since writing the above, mention of an experiment has been found which is perhaps the best proof of the theory advanced. Baubigny (*Compt. rend.*, **94**, 961, 1183, 1251, 1417, 1473, 1595, 1715 ; **95**, 34) found that neutral solutions of the salts of nickel are completely precipitated by hydrogen sulphide in one month's time. This shows that the formation of the sulphide takes time and that its non-formation is due to the fact that the process is too slow to be observed during an ordinary analytical precipitation. In the same way it is probable that acid would dissolve the sulphide in the course of time, even when it has no effect as ordinarily attempted.

[2] A method for the determination of S ions in general is the subject of an investigation in the laboratory now, and if results are obtained this comparison will be made.

Mols. per liter.

Nickel dichloracetate, concentration ············ 0.253
Dichloracetic acid ······························· 0.1424
Nickel salt precipitated as nickel sulphide······ 0.00722
Dichloracetic acid formed ······················· 0.0144
Nickel salt remaining in solution ··········· ··· 0.24

Mols. per liter.

Nickel acetate, concentration ···················· 0.071
Hydrochloric acid ······························· 0.78
Nickel salt as nickel sulphide··················· 0.019
Nickel salt left in solution····················· 0.052

The acetic acid formed in these cases was neglected on
account of its slight dissociation.

Mols. per liter.

Nickel acetate, concentration ···················· 0.0624
Hydrochloric acid ······························· 0.083
Nickel salt as nickel sulphide··················· 0.003
Nickel salt left in solution ···················· 0.0594

Mols. per liter.

Nickel acetate, concentration···················· 0.0788
Hydrochloric acid ······························· 0.0807
Nickel salt as nickel sulphide ·················· 0.0139
Nickel salt left in solution····················· 0.0649

Mols. per liter.

Nickel acetate, concentration···················· 0.0723
Hydrochloric acid ······························· 0.079
Nickel salt as nickel sulphide ·················· 0.0112
Nickel salt left in solution····················· 0.0601

Although the solubility products of the metallic sulphides are
unknown there is one way in which we may get an approximate
relation between them. Zengelis[1] has determined the electro-
motive force of several kinds of metal ions in contact with tenth-
normal solutions of potassium sulphide. Neumann[2] has deter-
mined the electromotive force of all the metals in their salt solu-
tions. By combining these measurements by the method of
Ostwald[3] it is possible to find the ionic concentrations of the
metals in contact with the same, but an unknown amount of $\overline{S}$
($\overline{HS}$) ions. For each metal we have a certain solubility-
product; i. e.,

$$M \times S = K,$$

[1] Ztschr. phys. Chem., 12, 311.
[2] Ibid., 14, 215.
[3] Lehrbuch d. allg. chem., III, 881.

where S and K are unknown. S, however, is the same in the case of all metals ; *i. e.*, the concentration of $\overline{\overline{S}}$ ions in a tenth-normal solution of potassium sulphide, hence the solubility-products will be proportional to the ionic concentrations of the metals in the potassium sulphide solution.   Using this method, a few relative solubility-products have been determined, and they serve to show the great difference between the metals of the iron group and those of the copper group.[1]

<div style="text-align:center">

Nickel············	0.0191	Concentration of metal ions in
Cobalt···········	0.0034	mols. per liter in presence of
Copper ··········	0.00021	the $\overline{S}$ ($\overline{HS}$) ions contained
Lead ·············	0.000024	in a tenth-normal solution of
		potassium sulphide.

</div>

Zinc, which is completely precipitated by hydrogen sulphide in acetic acid, should have a product still smaller than cobalt, which is not.   Cobalt and zinc show the disappearance of the anomalous behavior, cobalt having it to a smaller extent than nickel, and zinc not showing it at all.   We see from the results that the solubility-product of nickel sulphide is about 100 times greater than that of copper sulphide and 1000 times greater than that of lead sulphide.   This means that equal amounts of solution, containing the same ionic concentration of metal ions, will be precipitated when the concentration of $\overline{S}$ ($\overline{HS}$) ions for nickel, copper, and lead are in the ratio

<div style="text-align:center">

1000 : 100 : 1.

</div>

There is still one point to be considered in the behavior of nickel and cobalt sulphides.   When the sulphides of nickel, cobalt, and zinc are treated with dilute hydrochloric acid, the zinc dissolves, leaving the sulphides of cobalt and nickel behind, notwithstanding the fact that in water zinc sulphide is more insoluble than these.   This is also quite easily explained and depends simply upon the salt solution which is formed.   When a sulphide is dissolved in acid, as has already been mentioned, the ions of $\overset{+}{H}$ and $\overline{S}$ ($\overline{HS}$) unite to form hydrogen sulphide.   This

[1] Other determinations of the relative solubility-products are being made, and it is proposed to find also the absolute values by comparison with the value of one of the more soluble salts, determined by the method of the electrical conductivity.

removes the $\overset{-}{S}$ $(\overset{-}{HS})$ ions of the sulphide from the solution so
that more salt dissolves and has its ions removed in the same
way. Finally, we have a salt of the metal and hydrogen sul-
phide gas. The salt formed, if largely ionized, will prevent the
sulphide from giving off enough $\overset{-}{S}$ $(\overset{-}{HS})$ ions to reach with the
$\overset{+}{H}$ of the acid, the solubility-product of hydrogen sulphide ;
while if but slightly ionized this effect will not be noticed. The
whole process is similar to that of the formation of sulphide from
a neutral salt, when the acid formed prevents the hydrogen sul-
phide from dissociating to an extent sufficient to cause the solu-
bility-product of the sulphide to be exceeded. This is the pro-
cess which takes place when we attempt to dissolve the sulphides
of nickel, cobalt, and zinc in dilute hydrochloric acid. The chlo-
rides of nickel and cobalt are nearly completely ionized ; *i. e.*, the
conductivity is found to be almost constant for all dilutions. If
then a small amount of the chloride of nickel or cobalt is formed
it will prevent any more being produced. In the case of zinc
sulphide, however, the ionization is not so great, and, in addi-
tion, the solution is hydrolytically dissociated to a great extent.
Since hydrolytic dissociation removes zinc ions from the solution,
less of the depressing effect upon the solubility of the zinc sul-
phide is observed and it dissolves. In this way nickel and cobalt
sulphides do not dissolve in acid in which zinc sulphide is solu-
ble, since the solubility of these is depressed by the small portion
which may dissolve; zinc sulphide, on the contrary, retaining its
original solubility, dissolves. As a direct consequence of this
the nickel and cobalt sulphides should be formed from the chlo-
rides more readily than zinc sulphide. There are undoubtedly a
number of examples of this process where the relation of solubility
is reversed, but it is believed that this is the first one in the case of
a salt to be observed. If it were possible to find a salt of nickel
and cobalt which is ionized to a lesser degree than the corre-
sponding one of zinc, then, if the latter were not hydrolytically
dissociated, the relation in regard to solubility would be the same
in the acid, which would form that salt, as in water.

ON THE DETERMINATION OF ADDED WATER IN MILK.

BY A. G. WOODMAN.

IN order to estimate the amount of water which has been added to a sample of milk, it is generally necessary to make separate determinations of the specific gravity, the total solids, and the fat. The accurate determination of at least two of these factors is a matter of considerable time, and, although it is possible to shorten the time to a certain extent by the use of such formulas as those of Fleischmann, or of Hehner and Richmond, there can be no doubt that a rapid, and at the same time accurate, method for determining the extent to which milk has been watered would find extensive application.

The most successful of the various methods by which it has been proposed to effect this direct determination of added water are based, in general, upon the fact that under certain conditions the serum or liquid portion of sour milk possesses a fairly constant composition, much more so than the milk itself. The methods by which the milk serum is obtained depend for the most part upon the coagulation of the milk by means of dilute acid. Vieth[1] recommends letting the milk sour spontaneously by standing at the room temperature for two or three days and then separating the serum from the coagulum at 65° C. Other investigators prefer to coagulate the milk directly by the addition of an acid. Dietsch[2] and Radulescu[3] use dilute acetic acid and warm the milk. Reich[4] recommends the use of a small quantity of glacial acetic acid and final heating of the milk to 100° C. Sambuc[5] heats the milk to 40°–50° with two cc. of an alcoholic solution of tartaric acid of a specific gravity of 1.030–1.032, approximately the same as that of the milk serum itself. The whole question has been investigated quite thoroughly by Radulescu, who has made a study of the conditions necessary in regard to the strength of acetic acid employed, the temperature

[1] Forschungen auf dem Gebiete der Viehhaltung und ihrer Erzeugnisse, *1884*, (15), 334.

[2] *Chem. Ztg.* (*1884*), 323.

[3] Mitt. aus dem pharm. Ins. und Laboratorium für ang. Chem. der Univ. Erlangen, (*1890*), III, 93.

[4] *Milch Ztg.*, (*1892*), 274.

[5] Jour. de Pharm. et de Chim., (*1884*), 95.

to which the mixture should be heated, and the time required, in order to obtain satisfactory results. The method recommended by Radulescu is as follows: To 100 cc. of the milk is added two cc. of twenty per cent. acetic acid, and the mixture is heated in a water-bath at 85° C. for five or six minutes, as a result of which the casein separates in the form of a compact cake and is easily filtered off. After being thoroughly mixed the filtrate is cooled to 15° C. and its specific gravity taken. The acid used is variously stated in different portions of Radulescu's paper to be "twenty per cent. acetic acid," "twenty-five per cent. acid," and acetic acid having a specific gravity of 1.0294, which is about twenty-two per cent. strength. In the determinations which I have carried out, using practically the same method as that proposed by Radulescu, I have found that for the richer samples of milk the twenty per cent. acid is too dilute, failing to entirely precipitate the casein, but that the acid of twenty-five per cent. strength is sufficient in all cases.

After a number of experiments, following at first as nearly as possible the procedure recommended by Radulescu, subsequently making such modifications in the method as were found advisable in order to secure more nearly uniform results, I have adopted the following procedure: 100 cc. of the milk, which should be at a temperature of about 20° C., are thoroughly mixed with two cc. of a twenty-five per cent. solution of acetic acid, specific gravity 1.0350, in a small beaker. The beakers, kept covered with watch-glasses, are heated for twenty minutes in a water-bath kept at a temperature of 70° C., the temperature of the milk samples being brought gradually by this means to about 65° C. The beakers are then removed from the water-bath and placed immediately in ice-water, where they are allowed to remain for ten or fifteen minutes, after which the solutions are filtered through small, dry, plaited filters, the first portion of the filtrate, which generally comes through cloudy, being returned to the filter. After the filtrate has been thoroughly mixed it is cooled to 15° C. and its specific gravity taken by means of a Westphal balance. It occasionally happens, more especially with normal milk or milk to which only a slight amount of water has been added, that the serum which is thus obtained has a slight cloudiness or opalescence, but I have not

observed that it causes any appreciable difference in the specific gravity. For assistance in studying the conditions upon which the above procedure is based, I am indebted to Mr. J. W. Brown and Miss J. H. Bartlett.

In the following table (Table I) will be found the results obtained on samples of pure milk obtained from various sources, and on mixtures of these milks containing varying percentages of water, by the method that I have outlined above. All determinations of specific gravity have been made at $15°$ C., using a delicate Westphal balance, which gave the specific gravity of pure water at $15°$ C. as 1.0000.

TABLE I.

Specific Gravity.

Serum.

No.	Milk.	Normal.	Ten per cent. water.	Twenty per cent. water.	Thirty per cent. water.	Forty per cent. water.	Fifty per cent. water.
1·····	1.0337	1.0297	1.0263	1.0237	1.0206	1.0180	1.0153
2·····	1.0334	1.0294	1.0260	1.0232	1.0203	1.0174	1.0151
3·····	1.0340	1.0295	1.0264	1.0232	1.0206	1.0175	1.0151
4·····	1.0324	1.0293	1.0259	1.0233	1.0202	1.0178	1.0148
5· ···	1.0336	1.0296	1.0262	1.0235	1.0205	1.0177	1.0153
6·····	1.0328	1.0293	1.0258	1.0233	1.0202	1.0174	1.0148
7·····	1.0334	1.0292	1.0260	1.0233	1.0202	1.0175	1.0149
8·····	1.0325	1.0294	1.0260	1.0234	1.0201	1.0175	1.0152
9·····	1.0339	1.0296	1.0262	1.0236	1.0206	1.0178	1.0153
10·····	1.0335	1.0296	1.0261	1.0235	1.0204	1.0174	1.0148
11·····	1.0329	1.0292	1.0259	1.0234	1.0203	1.0173	1.0148
Av····	1.0335	1.0294	1.0261	1.0234	1.0204	1.0175	1.0150

The specific gravity of the serum from milk at a given dilution is shown by the table to be a fairly constant quantity, the average decrease for each ten per cent. of water being 0.0031.

The specific gravities given in Table I were obtained on samples in which the per cent. of water *in the mixture* varied by ten. As might naturally be expected, if the results are calculated on the basis of percentage of *added* water the differences in specific gravity are not so great. In Table II are given the results obtained on samples of pure milk to which varying percentages of water have been added.

TABLE II.

Samples varying by ten per cent. *added* water.

Specific Gravity.
Serum.

No.	Milk.	Normal.	Ten per cent. water.	Twenty per cent. water.	Thirty per cent. water.	Forty per cent. water.	Fifty per cent. water.
1....	1.0336	1.0294	1.0259	1.0239	1.0219	1.0199	1.0189
2....	1.0333	1.0295	1.0260	1.0240	1.0220	1.0200	1.0190
3....	1.0334	1.0294	1.0259	1.0239	1.0220	1.0200	1.0190
4....	1.0330	1.0295	1.0260	1.0239	1.0221	1.0201	1.0190
5....	1.0324	1.0294	1.0259	1.0239	1.0220	1.0199	1.0190
6....	1.0328	1.0294	1.0260	1.0239	1.0220	1.0200	1.0190
7....	1.0340	1.0294	1.0260	1.0239	1.0220	1.0200	1.0190
8....	1.0337	1.0296	1.0261	1.0240	1.0221	1.0201	1.0190
9....	1.0330	1.0294	1.0259	1.0239	1.0221	1.0200	1.0190
10....	1.0335	1.0295	1.0260	1.0239	1.0220	1.0199	1.0189
Av ...	1.03327	1.02945	1.02597	1.02392	1.02202	1.01999	1.01898

These results confirm the conclusion reached by Radulescu, that the specific gravity of the serum from normal milk is never below 1.027, and in no case of those examined was it found to be below 1.0290. The decrease in specific gravity caused by the addition of ten per cent. of water varied from 0.0035 to 0.0010. The statement is made by Radulescu,[1] that the addition of each ten per cent. of water to normal milk lowers the specific gravity of the serum by 0.0005 to 0.0010 and this value is also given by König.[2] This is evidently an error, for from the preceding table it will be seen that the decrease actually obtained is considerably higher and as a matter of fact the differences shown in Radulescu's tabulation of results vary from 0.0029 to 0.0012. I do not consider it advisable to determine the amount of total solids and of fat in the milk serum, as recommended by Radulescu, because if this is done the method offers no special advantages as far as regards economy of time and ease of execution over those ordinarily used.

The method as originally proposed by Radulescu has been criticised by E. Reich[3] on the ground that only a partial clarification of the milk is effected, the precipitation and removal of the albumen not being complete at the temperature to which the

[1] *Loc. cit.*

[2] Die Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, Ed. (*1898*), 361.

[3] *Milch Ztg.*, (*1892*), 274.

mixture is heated.   The following modification of the method
has been proposed by Reich : 100 cc. of the milk is thoroughly
shaken in a 200 cc. flask with four-tenths cc. glacial acetic acid,
the mixture heated for five or six minutes at 60°–65°, cooled, and
the liquid portion poured off into fifty cc. Erlenmeyer flasks.
These are hung for five or six minutes in a boiling water-bath,
then rapidly cooled in ice-water.   The casein and albumen are
removed by filtering through a small dry Swedish filter and the
specific gravity of the filtrate taken at 15° C.   I have determined
the specific gravity of the serum from five samples of milk
diluted with varying percentages of water by Reich's method
and also of the same samples by the modification of Radulescu's
method previously described.   These results are given in the
following Table (III):

<div align="center">TABLE III.</div>

<div align="center">Specific gravity.</div>
<div align="center">Serum.</div>

No.	Milk.	Normal.	Ten per cent. water.	Twenty per cent. water.	Thirty per cent. water.	Forty per cent. water.	Fifty per cent. water.
According to Radulescu's Method Modified.							
1......	1.0337	1.0294	1.0259	1.0239	1.0220	1.0199	1.0190
2......	1.0319	1.0294	1.0260	1.0240	1.0220	1.0199	1.0190
3......	1.0338	1.0295	1.0260	1.0239	1.0220	1.0200	1.0189
4......	1.0340	1.0294	1.0259	1.0239	1.0219	1.0200	1.0189
5......	1.0328	1.0294	1.0260	1.0240	1.0220	1.0200	1.0190
Same Samples According to Reich's Method.							
1......	1.0337	1.0293	1.0266	1.0240	1.0224	1.0205	1.0196
2......	1.0319	1.0289	1.0257	1.0234	1.0219	1.0200	1.0182
3......	1.0338	1.0292	1.0264	1.0245	1.0226	1.0207	1.0199
4.... .	1.0340	1.0296	1.0264	1.0243	1.0225	1.0205	1.0198
5......	1.0328	1.0295	1.0270	1.0247	1.0217	1.0210	1.0199

The claim of Reich that his method yields concordant results
which are uniformly lower than those obtained by Radulescu's
method is not borne out by the figures shown in the above table.
It has been my experience that the method offers no advantages
over that of Radulescu, being more tedious to carry out and
giving results which vary more widely.

As an illustration of the degree of accuracy with which the
amount of added water in milk may be estimated from the
specific gravity of the milk serum I give the following results

obtained on two samples purchased at a city grocery and sup-
posed to be pure milk :

	1.	2.
Specific gravity milk	1.0282	1.0263
" " " serum	1.0257	1.0234

The specific gravity of the serum indicated in one case ten per
cent. and in the other twenty per cent. of added water. The
amount of added water calculated from careful determinations of
the total solids and of the fat was very close to this, being 9.8
per cent. for the first sample and 19.6 per cent. for the second.
The method is easy to carry out and should prove to be of con-
siderable value.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
February, 1899.

DETERMINATION OF CALCIUM AND MAGNESIUM IN ASHES.[1]

BY J. K. HAYWOOD.

THOSE who have had any considerable number of ash samples
to analyze according to the method adopted by the Associ-
ation of Official Agricultural Chemists, cannot help having been
struck with the extreme difficulty of determining calcium and
magnesium. The whole trouble consists in washing the volu-
minous precipitate of basic acetate of iron and phosphate of iron,
which is not only so bulky as to be troublesome, but also com-
mences to run through the filter soon after washing is begun.

The following work was undertaken with the idea of showing
that this washing can be entirely done away with, without seri-
ously affecting the accuracy of the results. To do this the pre-
cipitation of the phosphoric acid and iron from the solution of
calcium and magnesium was made in a 500 cc. flask, the solu-
tion then cooled to room temperature, made up to the 500 cc.
mark, and *well shaken*. 250 cc. of this solution were then filtered
off through a dry filter, keeping the funnel covered to prevent
evaporation, evaporated to a small volume, ammonia added to
get rid of any small traces of iron that might have dissolved in

1 Read at the meeting of the Washington Section, March, 1899.

the liquor (nothing like the large amount that comes through
the filter when the precipitate is washed), and the solution again
filtered.   The manganese is removed with bromine and ammo-
nia, and calcium and magnesium determined in the filtrate.   It
will be noticed that this method does not correct for the volume
occupied by the precipitate of basic acetate of iron and phos-
phate of iron, and it was to show that this correction is imma-
terial that the following work was undertaken.

For purposes of analysis three powders were prepared : one
containing approximately ten per cent. of lime, three and five-
tenths per cent. of magnesia, and 86.5 per cent. of sand ; two
containing twenty per cent. lime, five per cent. of magnesia, and
seventy-five per cent of sand ; and three containing thirty per
cent. of lime, nine per cent. of magnesia, and sixty-one per cent.
of sand.   Ten grams of each powder were dissolved in hydro-
chloric acid and filtered to a volume of 500 cc., aliquot portions
being taken for analysis.

Analyses of the above powders showed the following per cents.
of calcium and magnesium oxides :

	I.	II.	III.
Lime············	9.81	19.74	29.78
	9.85	19.66	29.86
Average ········	9.83	19.70	29.82
Magnesia·······	3.69	5.28	8.90
	3.71	5.26	8.90
Average········	3.70	5.27	8.90

Aliquot portions were again taken from the solutions prepared
as above and phosphoric acid was added to each portion,
amounting in the case of solution I to five per cent. of the
total amount of powder used, in the case of solution II to ten
per cent. of the total amount of powder used, and in the case of
solution III to twelve per cent. of the total amount of powder
used.   Enough ferric chloride was added to precipitate all phos-
phoric acid, and these portions analyzed according to my method
mentioned above, with the following results :

	I.	II.	III.
Lime············	9.80	19.72	29.52
	9.76	19.80	29.54
Average ········	9.78	19.76	29.53

	I.	II.	III.
Magnesia········	3.75	5.21	8.95
	3.82	Lost	8.93
Average ········	3.79	5.21	8.94

showing practically the same results as those obtained above when no volume of a precipitate was neglected.

In the case of solution III a rather extreme case was next tried by adding enough phosphoric acid to correspond to twenty per cent. of the original powder. The results were :

III.

Lime ··········	29.74	Magnesia ··········	9.19
	29.90		9.21
Average ········	29.82		9.20

In my work last year on the official ash sample, which contained 9.83 per cent. of phosphoric acid, the calcium and magnesium were determined according to the above method with the following results, in triplicate :

Lime ··········	11.94	Magnesia ··········	5.83
	11.94		5.75
	11.97		5.77
Average	11.95		5.78

as against an average of lime 11.62, magnesia 5.74, by the other chemist engaged in the work.

The results obtained arranged in tabular form were :

No. 1.

	Lime.	Magnesia.
Before adding phosphorus pentoxide ·············	9.83	3.70
After adding five per cent. phosphorus pentoxide ·	9.78	3.79

No. 2.

	Lime.	Magnesia.
Before adding phosphorus pentoxide ·············	19.70	5.27
After adding ten per cent. phosphorus pentoxide ·	19.76	5.21

No. 3.

	Lime.	Magnesia.
Before adding phosphorus pentoxide ·············	29.82	8.90
After adding twelve per cent. phosphorus pentoxide ·······························	29.53	8.94
After adding twenty per cent. phosphorus pentoxide ·······························	29.82	9.20

	Lime.	Magnesia.
Washing precipitate	11.62	5.74
Not washing precipitate..........................	11.95	5.78

In the case of ashes which contain a larger per cent. of phosphoric acid than that included in the limits of this paper, a small correction may be necessary for the volume occupied by the precipitate. On account of lack of time I will reserve the investigation of this subject for a future paper.

THE EFFECT OF DI-IONIC ELECTROLYTES ON THE SOLUBILITY OF TRI-IONIC ELECTROLYTES WITH DIFFERENT IONS.[1]

BY ARTHUR A. NOYES AND EDWARD S. CHAPIN.
Received March 3, 1899.

1. THE OBJECT OF THE INVESTIGATION.

THE theory of the effect of one di-ionic electrolyte upon the solubility of another with different ions has already been developed by Noyes[2], and confirmed by our researches[3] and those of Noyes and Schwartz.[4] The solubility of tri-ionic electrolytes in the presence of other electrolytes with an ion in common has also been investigated.[5] The solubility of tri-ionic electrolytes in the presence of other electrolytes with different ions has, however, heretofore not been considered, except from a purely theoretical standpoint. The object of this article is to discuss theoretically a special case of this phase of solubility effect, and to communicate experiments, which confirm the theory. The special case chosen is the solubility of calcium hydroxide in the presence of ammonium chloride, in which case a weakly dissociated substance, ammonium hydroxide, is formed by metathesis.

2. THEORY OF THE SOLUBILITY EFFECT.

Consider a solution of any di-ionic electrolyte, CD, which is saturated with a tri-ionic electrolyte, AB_2. In accordance with the reaction

$$AB_2 + 2CD = AD_2 + 2CB$$

[1] Read at the Boston Meeting of the American Chemical Society, August 25, 1898.
[2] Ztschr. phys. Chem., 27, 267.
[3] This JOURNAL, 20, 751.
[4] Ibid., 20, 742.
[5] Ztschr. phys. Chem., 9, 623 ; 26, 152.

certain quantities of the undissociated substances AD_2 and CB will be formed, so that the solubility of AB_2 will be greater than that in pure water; for it exists in the solution not only in the form AB_2 and its ions (as in pure water), but also in the form AD_2 and CB. Suppose that the substances CD and AD_2 are strongly dissociated, in which case their undissociated amounts may be determined with sufficient exactness from their electrical conductivities;[1] and suppose that the substance CB on the contrary is only slightly dissociated, and that it conforms to the laws of mass action. Designate the molecular concentrations of the ions A, B, C, and D by the same capital letters; the molecular concentrations of the undissociated portions of the four substances AB_2, CD, AD_2, and CB by a, b, c, and d respectively; the solubility of AB_2 in pure water by m_0; the corresponding degree of its dissociation by a_0; the solubility of AB_2 in a solution of CD of concentration n by m; the product 4 $m_0^2 a_0^2$ by k_a; and the dissociation constant of CB by k_d. The two following equilibrium equations then hold true, the first expressing the constancy of the product of the concentrations of the ions of any tri-ionic salt with which a solution is saturated, and the second the relation between the concentration of the undissociated portion and those of the ions of any di-ionic salt.

$$A \times B^2 = k_a \tag{1}$$
$$C \times B = k_d d \tag{2}$$

From the conditions of the case the three following equations may be derived:

$$A + a + c = m \tag{3}$$
$$B + 2a + d = 2m \tag{4}$$
$$C + b + d = n \tag{5}$$

These five equations contain only five unknown quantities A, B, C, d, and m, and can therefore be solved for m. For brevity we substitute

$$x = m - a, e = n - b \text{ and } r = \frac{4 k_d^2}{k_a}.$$

After elimination the following equation is obtained:

$$rx^4 - (2 rc + 4)x^3 + (rc^2 + 4e + 4 c)x^2 - [(k_d + e)^2 + 4 ec]x + [c(k_d + e)^2 + k_a] = 0, \tag{6}$$

1 *Ztschr. phys. Chem.*, 27, 270.

an equation, which after the substitution of the numerical values, may be solved in the usual manner. The method of calculating the values of b and c (here considered to be known) will be explained later by an example.

When the solutions of AB_2 or of CD are very dilute, or when in the case of moderately concentrated solutions approximate values only are desired, the values of b and of c may be neglected, and the equation becomes

$$rx^4 - 4x^3 + 4nx^2 - (k_d + n)^2 x + k_a = 0. \qquad (7)$$

When, on the contrary, as in the case to be considered, the substance AB_2 is moderately soluble, the concentration of CD is considerable, and the substance CB is slightly dissociated—the values r, k_d, and b are negligible, while c is appreciable. The equation then becomes

$$4x^4 - 4(n + c)x^2 + (n^2 + 4nc)x - (cn^2 + k_a) = 0. \quad (8)$$

3. DESCRIPTION OF THE EXPERIMENTS.

In order to test these principles, we have determined the solubility of calcium hydroxide in water and in three ammonium chloride solutions of different concentrations. The calcium hydroxide was prepared from a supposedly pure sample of the same by dissolving in hydrochloric acid, treating with ammonium hydroxide to remove other metals, precipitating with ammonium carbonate, and igniting this precipitate just before using in small portions in a platinum crucible. The ammonium chloride was prepared by precipitating with strong hydrochloric acid, a concentrated solution of the commercial article, and three times re-crystallizing the product from hot water. Two solutions of ammonium chloride, each about 0.087 normal, were prepared independently. From these were prepared by dilution solutions of one-half and one-fourth the original concentration. The concentrations of the strong solutions were determined gravimetrically by precipitation with silver nitrate.

The solutions were saturated in the usual manner.[1] As they would not settle, they were filtered.

On account of the tendency of the calcium hydroxide to absorb carbon dioxide from the air, this was done in air free from this gas within a vacuum desiccator containing potassium hydroxide.

[1] *Ztschr. phys. Chem.*, 9, 603.

The apparatus was so arranged that the saturated solutions were sucked from the bottles in which saturation took place directly into the desiccator through a hole in the top onto filters which stood in graduated flasks. The flasks were filled a little over the mark. The desiccator was then opened, the liquid in the flasks was brought exactly to the mark with filter-paper and was then emptied into Erlenmeyer flasks containing not quite enough standard hydrochloric acid to neutralize the dissolved calcium hydroxide. The titration was then quickly completed with more hydrochloric acid, using methyl orange as an indicator.

4. THE EXPERIMENTAL RESULTS.

The following table contains the values of the solubility of the calcium hydroxide at $25°$ expressed in millimols (thousandths of a molecular weight) per liter.

Exp. No.	Conc of NH_4Cl 0.0.	Conc. of NH_4Cl 21.76 millimols.	Conc. of NH_4Cl 43.52 millimols.	Conc. of NH_4Cl 87.03 millimols.
I	20.24	28.99	39.12	59.45
2	20.21	29.09	39.31	59.96
3	20.23	29.06	39.31	59.60
4	20.26	29.13	39.22	59.67
5	20.14	29.13	39.30	59.74
Mean	20.22	29.08	39.23	59.68

In order to test the theory, it is necessary to know in addition to these solubility values, the degree of dissociation of the substances involved. In the case of ammonium chloride, calcium chloride, and ammonium hydroxide, reliable measurements of their electrical conductivities had been previously made ; but in the case of calcium hydroxide in pure water, there were no data available, and therefore we have measured it ourselves. The solutions were saturated in the rotating apparatus, and their conductivities were then measured by the usual method of Kohlrausch. The value of the molecular conductivity of a 0.02022 molecular solution of calcium hydroxide was found to be 400.7[1] at $25°$. This corresponds to a degree of dissociation of 0.808, if according to Kohlrausch[2] (μ_∞ (OH) $= 186$) and to Bredig[3] (μ_∞(Ca) $= 124$), 496 is assumed as the limiting value of the molecular conductivity of calcium hydroxide.

[1] Two independent solutions gave 400.5 and 400.9.
[2] Wied. *Ann.*, **50**, 408. Kohlrausch gives 165 as the value for μ_∞(OH) at $18°$ from which, and from the temperature coefficient, follows the value 186 at $25°$.
[3] *Ztschr. phys. Chem.*, **13**, 235.

5. CALCULATION OF THE THEORETICAL VALUES AND COMPARISON OF THEM WITH THE EXPERIMENTAL ONES.

We have calculated the theoretical values by equation (8); for the value of r (0.000085) and that of k_d (0.000019), are extremely small, and that of b, even in the most concentrated solution (about one-tenth normal) is but $0.001 \times n$. The small value of b, the quantity of undissociated ammonium chloride, is explained by the fact that the concentration of the ammonium ions, on account of the weakness of the ammonium hydroxide, is extremely small. The constant k_a ($= 4m_0^3 a_0^3$) which appears in the equation is equal to 0.00001748; for according to our experiments $m_0 = 0.02022$, and $a_0 = 0.808$. The value of c, the undissociated quantity of calcium chloride, varies with the value of n. In order to determine the value of c in the different cases, we have made use of the conductivity measurements of MacGregory.[1] From his data at the concentrations 0.01, 0.05, and 0.1 normal we calculated first the degree of dissociation by dividing by the limiting value ($\mu_\infty (\frac{1}{2} \text{CaCl}_2) = 110$), and then the empirical dissociation constant k_c' by van't Hoff's[2] formula,

$$k_c' = \frac{c_i^3}{c_s^2},$$

where c_i represents the concentration of the ions and c_s that of the undissociated substance. From this constant the values of c may then be calculated conversely with sufficient exactness by the equation:

$$k_c' = \frac{A \times D^2}{c^2},$$

in which A may be put equal to x (an estimated value of x being used) and D equal to n. The values of c thus calculated are: 0.0032 for $n = 0.0217$; 0.0074 for $n = 0.0435$; and 0.0180 for $n = 0.087$. They are, therefore, appreciable quantities.

The following table contains the calculated solubilities together with those found by experiment, both expressed in millimols per liter.

[1] Phys. Review, 2, 370.

[2] Ztschr. phys. Chem., 18, 300.

Concentration of ammonium chloride.	Solubility of calcium hydroxide. Found.	Calculated.
0	20.22	....
21.76	29.08	28.09
43.52	39.23	38.6
87.03	59.69	58.3

The agreement is satisfactory.   The theory developed regarding the effect of di-ionic electrolytes on the solubility of tri-ionic electrolytes with different ions is therefore confirmed.
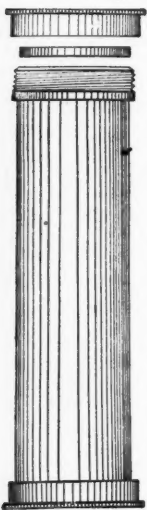
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, March, 1899.

MEASUREMENTS OF " TURBIDITY" IN WATER.

BY W. P. MASON.

THE method of expressing turbidity in words is so unsatisfactory that the writer has for some time past employed the following means of securing numerical results : The change has proved of decided advantage, particularly for an examination of filtrates and storage waters. Use is made of a brass tube two and one-half inches in diameter and two feet long, closed at the ends by disks of quarter-inch plate glass held in place by screw-caps.[1] Such tubes are easily cleaned and give excellent satisfaction.

For the purpose of measuring the amount of turbidity, a standard is prepared, consisting of one gram of exceedingly fine kaolin (obtained by elutriation) suspended in one liter of distilled water.   Each cubic centimeter of this preparation will contain one milligram of suspended clay.

Having nearly filled the duplicate observation-tube with distilled water, enough of the "clay standard" is added to make the turbidity equal to that of the water under examination in the other tube.   Knowing the volume of water operated upon and the amount of "clay standard" used, the turbidity expressed in parts per million can readily be calculated. It should be noted that although the tube containing the "clay standard" is, of necessity, not completely full, yet by inclining

1 Such tubes may be obtained from Richards & Co., 30 East 18th St., New York City.

its barrel towards a horizontal position the required observation depth of two feet is easily obtained.

Any quickly subsiding material present should be classed as sediment rather than turbidity. To determine the same it would be best to decant the water above such deposit and then catch it upon a weighed filter or in a Gooch crucible.

THE TOXIC ACTION OF SODIUM FLUORIDE.[1]

By Herbert B. Baldwin.

Received April 10, 1899.

THE title of this article was suggested by a recent case of accidental poisoning by means of sodium fluoride. The substance is now largely sold as an insecticide put up in tin cans resembling baking-powder boxes. In this way and on account of its now somewhat extended use in the arts there is considerable liability of accidental poisoning from it. The possibility of future accidents, and the fact that in searching for literature on the salt as a toxic agent no record was found of any severe or fatal poisoning, induced the writer to present a brief history of the case together with such other information as could be collected.

Some pan-cakes served for breakfast were partaken of by six or seven persons. Some ate very sparingly, one woman only a portion of one, while one man ate three or four of them. All who had eaten vomited within five to fifteen minutes afterward. In some cases purging occurred, in others it did not. In one case, at least, this purging and occasional vomiting continued for a day or more, with pains in the limbs complained of.

In the case of the man who ate three or four cakes, vomiting commenced early, but he soon recovered sufficiently to attend to his duties as bartender until early in the afternoon when he was obliged to retire to his room. He died early in the evening of the same day, practically without medical attendance. Further symptoms in the case could not be ascertained.

At the time this occurred it was supposed to be a case of criminal poisoning and some milk used in mixing the cakes was suspected. An analysis, by the writer, of this milk and a portion of the viscera of the deceased failed to detect any of the usual mineral poisons. But a small amount (0.007 gram) of what

[1] Read at the meeting of the New York Section, April 7, 1899.

looked like ordinary white sand was separated and preserved.

Further investigation by the authorities resulted in finding a box of roach poison by the side of the baking-powder box and an analysis showed it to consist of sodium fluoride which contained as an impurity a small amount of sand which was microscopically identical with that recovered from the stomach of the deceased.

This served as a clue, and although the contents of the stomach had been destroyed, a little mucus scraped from a small portion of tissue that had remained in the laboratory for six weeks, contained enough of the poison to be detected with certainty.

The mucus was macerated with a little water and filtered. The filtrate was precipitated with calcium chloride and a very small precipitate (probably two or three milligrams) of calcium fluoride obtained. This, after drying, was sufficient, when mixed with a fraction of a drop of sulphuric acid, to strongly etch a piece of glass. The sodium was detected before precipitating by means of flame coloration and the spectroscope.

There was no means of knowing exactly what the fatal dose had been in this case, but judging from the relative amounts of sand in the stomach and the roach poison, it must have been at least ten grams.

The stomach was nearly empty and contained only a small amount of a gray slimy mucus that clung rather tenaciously to the mucous membrane which was somewhat inflamed.

While the above investigation was in progress an almost identical accident occurred in another city. Here fairly accurate data were obtainable regarding the dose and symptoms.

About twenty-six grams of the fluoride were used instead of baking-powder in making twenty-six wheat cakes for breakfast. One brother ate nine, a daughter six, the mother (age sixty-nine) five and another brother one. Assuming the substance to have been thoroughly mixed, the amount taken by each was, respectively, nine, six, five and one grams.

The symptoms varied considerably as follows: The man who had taken nine grams was seized with very violent cramps almost immediately afterward. These continued at frequent intervals for about thirty-six hours and were followed by severe pain for

three or four days before recovery.   Purging commenced quite early and vomiting in about four hours.   Retching continued for two or three days.

The daughter who had taken six grams felt sick when eating the last cake and vomited in five or ten minutes.   Sometime afterward she took some mustard water and vomited again. She felt weak and sick for two days.   No diarrhea.

The mother took but five grams but was the most seriously affected of all.   Although the nauseous feeling commenced, as with the others, within five minutes, she did not vomit for about five hours.   Diarrhea, however, began in fifteen or twenty minutes and was a serious symptom for several days.   She was confined to her bed for two weeks with extreme prostration and did not completely recover for four weeks.

Information regarding the heart and lungs could not be obtained in any of these cases.

Three other cases were heard of.   One was a man who was made to vomit by merely tasting the substance a few times with the object of finding out whether it was borax or not.   Another one (a salesman) had tasted the salt many times a day without any ill effects.   The other case was a man who, while intoxicated, took in mistake for Rochelle salts about fifty grains.   He was soon taken with violent vomiting and purging but recovered in a few days.

Before these last cases cited came to the knowledge of the writer and before any literature on the subject had been found, he made the experiment of taking a few gradually increased doses of sodium fluoride to ascertain its toxic action upon himself.   Merely tasting small quantities produced a slight feeling of nausea with slight salivation.   0.03 gram swallowed with some bread produced no effect.   Neither did 0.09 gram taken one hour later, except a little salivation.   0.25 gram, however, taken two days afterward on an empty stomach, produced nausea in two minutes.   This gradually increased in severity for twenty minutes when the period of greatest intensity was reached.   There was a largely increased flow of saliva and some retching but no vomiting occurred at that time although the desire was very great.   The nausea gradually subsided so that luncheon could be eaten (without relish), but vomiting took

place immediately on its completion which was two hours after taking the poison. Slight nausea continued throughout the following day but disappeared on the second day.

Although some of the toxic properties of sodium fluoride have long been known, no reference was found in the literature of anyone who had taken a large dose of it. This is probably due to its very limited commercial use in former days.

As long ago as 1867 Rubuteau[1] in experiments on dogs and rabbits found that in dogs five-tenths gram given by the mouth made them sick but that 0.25 gram was without action. One gram injected into the blood caused serious symptoms but was not fatal. In rabbits 0.25 gram by the mouth made them sick and the same amount injected was fatal.

These results do not agree, as regards the lethal dose, with similar experiments made later by others, and Rubuteau afterward says that the purity of the fluoride used was questionable.

Kolipinski[2] in 1886 used it medicinally with good results in sympathetic headache, intermittent fever and epilepsy in doses of less than a quarter of a grain, larger doses being liable to cause nausea. He says "that five grains given to a dog on meat produces vomiting in a few minutes which continues until the stomach is empty, and may then cease or end a little later with much retching or ejection of mucus. * * *

"The intravenous injection of a toxic dose (three grains for the cat) produces in this animal and in the dog death in a few hours." * * * With the vomiting may occur evacuation of feces and urine. * * * At intervals there are moments of unrest with twitchings or tremors of the limbs. For the most part the animal is quiet and unconscious. This stage begins with the cessation of vomiting which ends within the first hour. * * * The urine is slightly albuminous and rich in fluorine."

The same authority describes an experiment where he gave at the same time to each of three males one-eighth of a grain of sodium fluoride. The urine voided at that time soon became turbid at the room temperature, while that passed two hours later remained clear for seven days from the perservative effect of the

[1] Étude experimentale sur les effets physiol. des fluorures. Paris, 1867.
[2] Med. News, 49, No. 8, Philadelphia, 1886.

fluorine eliminated.   Urine passed one to two hours afterward quickly decomposed as usual.

Shulz,[1] 1889, found that when subcutaneously injected, the lethal dose of sodium fluoride was for rabbits 0.2 to 0.4 gram, for dogs 0.3 gram and for frogs 0.005 to 0.006 gram.

Haidenhain,[2] 1889, stated that 0.05 to 0.10 gram for kilogram of body weight injected into the blood of dogs produced death.

Weinland,[3] 1894, in experimenting with the sodium salts of the halogens on mucous membrane from the throat of the frog found that equimolecular solutions killed the membrane in the following orders :   Sodium fluoride (two and one-tenth per cent.) in one minute; sodium iodide (seven and five-tenths per cent.) in ten minutes; sodium bromide in forty-five minutes, and sodium chloride (two and nine-tenths per cent.) in sixty minutes.

P. Grützner,[4] 1893, found the same order of sensitiveness for nerves.

Czrellitzer,[5] 1895, after reviewing the work of others, concludes that sodium fluoride is an active poison for micro-organisms of all kinds, algae, and nerves and muscles of the higher organisms. He proves that the poisonous action is stronger on some kinds of cells than others.   After citing the theories of several authors he believes there is no satisfactory explanation of the way in which it exerts its poisonous action.

It appears from the evidence thus far obtained that the most characteristic symptoms produced by sodium fluoride in the individual are early nausea, vomiting, and salivation.   Its detection may be accomplished, as in the case cited, by precipitating the solution with calcium chloride and testing the calcium fluoride obtained for fluorine.   The results of Kolipinski's experiments indicate that an examination of the urine would also be important in cases of suspected poisoning.

The facts ascertained seem sufficient to class sodium fluoride among the less violent poisons and as such it ought to find a place in works on toxicology.

[1] Untersuchungen über die Wirkung des Fluornatriums und der Flüssaure: Arch. f. exp. Path. und Ther., 1889.
[2] Neue Versuche über die Aufsaugung im Dündarm.—Pflüger's Arch., 1894.
[3] Ueber Chemische Reizung des Flimmerepithels.—Pflüg. Arch., 58, 1894.
[4] Ueber Chemische Reizung Motorische Nerven: Pflüg. Arch., 53, 1893.
[5] Zur Kentniss des Fluornatrium, Inaugural Dissertation, Breslau, 1895.

THE THEORY OF THE SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM FROM THE MIXED SULPHATES.

By J. Livingston R. Morgan.

A mixture of a soluble sulphate and carbonate transforms strontium and calcium sulphates into carbonates, leaving barium sulphate unchanged. Ammonium carbonate has also this same effect, so that the use of the soluble sulphate seems superfluous. The object of this paper is to show the action with both solvents, to calculate the effect of the sulphate added or formed, and also to show how the theories of physical chemistry may be applied to analytical chemistry. By Nernst's Laws,[1] for saturated solutions the undissociated portion of an insoluble salt remains constant even after addition of a salt with an ion in common. In the equation of equilibrium for a binary salt,

$$Kc = c_1 c_2, \tag{1}$$

where c is the concentration of undissociated salt (in gram-molecules per liter) and c_1 and c_2 are those of the two ions, K being the ionization constant; K and c are both constant for a saturated solution, hence

$$c_1 c_2 = \text{constant} = \text{solubility product.} \tag{2}$$

The meaning of this product may be expressed as follows: for any one constant temperature the two ions may exist free to such a concentration that the product just reaches this value. If we add to such a solution a salt with an ion in common, an undissociated portion is formed from equivalent amounts of the two ions, until the product of those remaining just reaches the value of the solubility product. The undissociated portion being increased by the addition, it is necessary that a certain amount of it separates out in the solid form, since the solution was saturated. In exactly the same way a substance is always less soluble in a solution containing an ion in common than it is in pure water. In such a case, one ion being present to a large extent, the substance can dissolve only so long as the product of the concentration of the one ion into the sum of those of the two portions of the other is less than or

[1] See Morgan and Gotthelf : This Journal, 21, 494.

equal to the solubility product. These relations are best shown by an alteration of equation 2; we have then,

$$c_1'(c_2' + x) = \text{solubility product,} \qquad (3)$$

when $c_1' = c_2'$ is the present solubility of the salt, in terms normal, and x is the concentration of the ions added, expressed in the same terms. When x and the solubility product are both known it is simple to find $c_1' = c_2'$; or when $c_1' = c_2'$ is known as well as the solubility product we can find x. In all cases where $c_1' = c_2'$ is very small and x is large, c_2' may be neglected as compared with x and we have

$$c_1'x = \text{solubility product.} \qquad (4)$$

In all cases of insoluble salts such as those used in an analysis, we may neglect the undissociated portion, and consider the major portion of the substance as present in the ionic state, for in such dilute solutions the undissociated portion, while still existing, must be exceedingly small.

By use of these equations, and especially (2) and (3), it is possible to calculate from the solubility of a substance in water its solubility product and also its solubility in presence of like ions of any definite concentration. The solubilities which form the basis of this paper are taken from Holleman.[1]

For the sulphates and carbonates of barium, strontium and calcium by (2) at 20° C., we have,

$$\overset{++}{Ba} \times \overset{--}{SO_4} = 0.0000000001 \qquad (5)$$

$$\overset{++}{Ba} \times \overset{--}{CO_3} = 0.0000000105 \qquad (6)$$

$$\overset{++}{Sr} \times \overset{--}{SO_4} = 0.00000029 \qquad (7)$$

$$\overset{++}{Sr} \times \overset{--}{CO_3} = 0.000000005 \qquad (8)$$

$$\overset{++}{Ca} \times \overset{--}{SO_4} = 0.0029 \qquad (9)$$

$$\overset{++}{Ca} \times \overset{--}{CO_3} = 0.0000000154 \qquad (10)$$

In saturated water solutions of these salts we have then ionic concentrations as follows :

$$\overset{++}{Ba} = \overset{--}{SO_4} = 0.00001 \text{ normal} \qquad (11)$$

$$\overset{++}{Ba} = \overset{--}{CO_3} = 0.0001 \quad \text{``} \qquad (12)$$

$$\overset{++}{Sr} = \overset{--}{SO_4} = 0.00054 \quad \text{``} \qquad (13)$$

[1] *Ztschr. phys. Chem.*, **12**, 125–139.

$$\overset{++}{Sr} = \overset{--}{CO_3} = 0.00007 \text{ normal} \qquad (14)$$

$$\overset{++}{Ca} = \overset{--}{SO_4} = 0.054 \qquad `` \qquad (15)$$

$$\overset{++}{Ca} = \overset{--}{CO_3} = 0.000124 `` \qquad (16)$$

We see from these results that the carbonates of strontium and calcium are less soluble than the sulphates, while for barium the relation is reversed. From the results already given it is quite simple to find the concentration of $\overset{--}{CO_3}$ ions necessary to form the carbonate from the sulphate. Thus for barium, by (6) and (11) we find that,

$$x = \frac{0.0000000105}{0.00001} = 0.00115 ;$$

i. e., it is necessary to have a minimum of 0.00105 gram-molecules of CO_3 ions to the liter to cause the solubility product of barium carbonate to be reached in a saturated solution of barium sulphate.

In a like manner we find values of $\overset{--}{CO_3}$ for strontium and calcium to be :

$CO_{3(Sr)} = x = \dfrac{0.000000005}{0.00054} = 0.0000092$ normal (by (8) and (13)).

$CO_{3(Ca)} = x = \dfrac{0.0000000154}{0.054} = 0.000000385$ normal (by (10)) and (15)).

These values would not cause the complete transformation of the sulphate into carbonate, but anything over them would cause some of the carbonate to be formed. It must always be borne in mind that an alkali sulphate is formed by the transformation, and that the $\overset{--}{SO_4}$ ions of this decrease the solubility of the insoluble sulphate so that equilibrium would be reached unless a sufficient excess of $\overset{--}{CO_3}$ ions are present. The relation between the effect of the $\overset{--}{SO_4}$ ions, and those of $\overset{--}{CO_3}$ may be readily calculated. Thus for barium sulphate, the solubility is depressed from 0.00001 normal to 0.000000001 normal by a tenth-normal solution of $\overset{--}{SO_4}$ ions; *i. e.*,

$$y + 0.1 = 0.0000000001.$$

$$y = 0.0000000001 = \text{concentration of } \overset{++}{Ba} \text{ ions.}$$

The amount of $\overline{\overline{CO}}_3$ ions necessary to cause the solubility product of the barium carbonate to be reached is then,

$$0.000000001 \times x = 0.0000000105$$
$$x = 10.5 \text{ normal.}$$

In other words a tenth-normal solution of $\overline{\overline{SO}}_4$ makes it necessary to add an equal amount of a 10.5 normal solution of $\overline{\overline{CO}}_3$ to cause the solubility product of barium carbonate to be reached, and until that concentration is exceeded no barium carbonate can be formed. The tenth-normal solution of $\overline{\overline{SO}}_4$ has not such a marked effect upon the formation of the carbonates of strontium and calcium. Thus :

$$\overset{++}{Sr} \times 0.1\,\overline{\overline{SO}}_4 = 0.00000029$$

$$\overset{++}{Sr} = 0.0000029 \text{ solubility of } SrSO_4 \text{ in presence of}$$
tenth-normal $\overset{++}{SO}_4$.

$$0.0000029 \times \overline{\overline{CO}}_3 = 0.000000005$$
$$\overline{\overline{CO}}_3 = 0.0017 \text{ normal.}$$

By this it is possible to explain the non-solution of barium sulphate in ammonium carbonate and in a solution of a sulphate and carbonate. In the case of ammonium carbonate acting upon the three sulphates, those of strontium and calcium form rapidly, even though the concentration of the $\overline{\overline{CO}}_3$ ions is small. The barium sulphate may also dissolve slightly, but the soluble sulphate formed during the reaction will soon prevent any further formation, and that formed from the strontium and calcium salts will cause the reverse transformation to take place, so that the barium sulphate transformed, will be formed again and its solubility decreased in proportion to the amount of $\overline{\overline{SO}}_4$ ions. Since our object is to make the precipitates as insoluble as possible it is always well to have an excess of the precipitant. According to Fresenius it is advisable to use a solution containing by weight one-third as much sulphate as carbonate. The carbonate and sulphate of potassium will then be related in terms normal as 1 : 0.4 ; and if we use a normal solution of potassium carbonate mixed with a 0.4 normal solution of potassium sulphate, the rela-

tion of the ions of $\overline{\overline{CO_3}}$ and $\overline{\overline{SO_4}}$ will be as 0.48 is to 0.21 normal. Absolutely no barium carbonate will then be produced and the solubility of the barium sulphate will be depressed to

$$\overset{++}{Ba} \times 0.21 = 0.0000000001$$
$$\overset{++}{Ba} = 0.0000000005 \text{ normal.}$$

The solubility of the strontium as well as of the calcium sulphate will be depressed but slightly.

$$\overset{++}{Sr} \times 0.21 = 0.00000029$$
$$\overset{++}{Sr} = 0.0000013 \cdot$$
$$0.0000013 \times \overline{\overline{CO_3}} = 0.000000005$$
$$\overline{\overline{CO_3}} = 0.004 = \text{amount necessary to form solubility}$$

product.

$$\overset{++}{Ca} \times 0.21 = 0.0029$$
$$\overset{++}{Ca} = 0.014$$
$$0.014 \times \overline{\overline{CO_3}} = 0.000000154$$
$$\overline{\overline{CO_3}} = 0.0000011 = \text{amount necessary to form solu-}$$

bility product.

And even with the soluble sulphate formed during the reaction the carbonates will be produced very rapidly. The speed of the transformation will in all cases be proportional to the difference between the concentration of the metallic ions from the carbonate and sulphate. The separation in presence of ammonium carbonate, then, is caused by the soluble sulphate formed during the reaction acting upon the barium sulphate, thus making it more insoluble, while it has practically no retarding effect upon the transformation of the other two sulphates. When one molecule of $\overline{\overline{SO_4}}$ is present with barium sulphate, it counteracts the influence of 105 molecules of $\overline{\overline{CO_3}}$. In the case of the mixture of carbonate and sulphate the amount of sulphate has but a slight depressing effect upon the strontium and calcium sulphates, while it depresses, to a very great extent, the solubility of the barium sulphate. The excess of $\overline{\overline{CO_3}}$ ions has the same effect upon the two carbonates so that the three salts are made as insoluble as possible and are separated by hydro-

chloric acid, the calcium and strontium being then separated by other reagents.

All the above, as far as concerns the carbonates, is modified slightly by the hydrolytic dissociation which takes place in the solutions. The relations, however, between the carbonates and sulphates will remain unchanged since the hydrolytic dissociation will take place to nearly the same extent in the solutions of all three.

REVIEW.

A BRIEF HISTORY OF THE MOVEMENT FOR INCREASING THE ACCURACY AND FOR IMPROVING THE CONSTRUCTION OF CHEMICAL MEASURING INSTRUMENTS.

The greater part of the matter contained in this paper was compiled for the use of the "Committee on Standards for Chemical Measuring Instruments" of this society and formed a part of that committee's report, which was read at the New York meeting in December last, and which is now before the committee for the reconsideration of some minor details, in accordance with a promise made to a minority of the committee. I may state, however, that the committee has unanimously agreed to the proposition that the society extend a formal invitation to the U. S. Office of Standard Weights and Measures to adopt regulations governing the construction, calibration, and testing of volumetric apparatus, similar to the regulations of the Kaiserliche Normal-Aichungs-Commission of Germany. This was the most important recommendation contained in the report of the committee as presented at New York, and it will soon be before the council of the society for action.

It is at the suggestion of my fellow members of the committee that I now present the following data in this form.

The Work of European Chemists.

As early as 1891, the "Deutsche Gesellschaft für angewandte Chemie" and the "Verein deutschen Eisenhüttenleute" had taken up the question of standards for chemical measuring instruments, and it was with the assistance and coöperation of these associations that the excellent regulations of the German Normal-Aichungs-Commission for testing volumetric apparatus were perfected and finally adopted. These regulations, as published in 1893, were as follows:

NOTICE IN REGARD TO THE TESTING OF CHEMICAL MEASURING FLASKS, ETC.

[From Zeitschrift für angewandte Chemie, 1893, pp. 557-559].

The Kaiserliche Normal-Aichungs-Commission published the

following directions, based upon article 18 of the regulations governing weights and measures (special supplement to Reich's Gesetzblattes, No. 30) :

I. Allowable Measuring Apparatus.

1. For exclusive use for chemical volumetric analysis of aqueous solutions, glass vessels will be admitted for testing as follows :

Vessels with one mark to hold a single volume.

(*a*) Flasks.

(*b*) Pipettes with upper suction tube and a lower delivery tube.

Vessels marked to hold a certain definite volume and certain subdivisions thereof.

(*c*) Measuring glasses (also called measuring cylinders, being measuring tubes having a foot).

(*d*) Burettes (measuring tubes without a foot, but with a delivery tube).

(*e*) Measuring pipettes (measuring tubes having a suction tube at the upper end and a delivery tube at the lower end).

2. The capacity of a measuring vessel is to be limited either by the mark or the lower opening, and its quantity is marked upon the vessel for a temperature of a vessel of 15° of the centigrade thermometer, in the liter, fractions of a liter, or in cubic centimeters, in which case the cubic centimeter is to be the 1-1000 part of a liter.

3. Measuring vessels may be graduated either to hold (*messgeräthe auf Einguss*) a given quantity to the mark, or to deliver (*messgeräthe auf Ausguss*) a given quantity. Measuring vessels provided with a device for the delivery of liquids must always be graduated to *deliver* the volume of liquid for which they are marked. Other vessels may be graduated to either hold or to deliver, but for only one of these purposes in the case of any single vessel. The volume of liquid is measured with a delivery apparatus by filling and emptying, with precautions to retain a uniformly unpreventable moistening of the walls of the vessel. This uniform moistening is insured by observing the following precautions:

(*a*) Measuring vessels which are emptied by turning up-side-down are held for one minute after emptying in an inclined position to allow them to drain, when the last drop is wiped off.

(*b*) In the case of pipettes the liquid is allowed to flow out entirely, or to the lower mark, according to the method of graduation, while the delivery tube is held without motion in contact with the sides of the receiving vessel. After the free outflow of the liquid has stopped, or after the lower mark has been reached, the pipette is allowed to drain for one-quarter of a minute.

(*c*) In the case of burettes, or measuring pipettes (pipettes graduated to deliver fractions of their maximum capacity), the desired quantity is drawn out, the last drop is removed, and the reading is taken off after waiting two minutes.

4. The cross-section of the measuring vessel must always be circular. The space occupied by the liquid to be measured, viewed in the direction of its greatest diameter, should decrease in size above and below, best at the same rate. Where the body of the vessel has a tube or cylindrical portion sealed on, the body of the vessel must gradually merge into the cylindrical portion without any abrupt change of direction, so that there will be no hindrance to the ready outflow of the liquid.

5. The mark shall be narrow, and both it and the label shall be plainly etched, ground, or applied in some other permanent manner. It should never be merely painted. The mark should always be upon a cylindrical, regularly formed, transparent part of the vessel. Coloring the mark is permitted.

6. The mark shall pass at least halfway around the vessel and lie in the plane to which the axis of the vessel is perpendicular.

7. In the case of measuring vessels marked for subdivisions of their total capacity, these subdivisions must all be equal.

8. Capacity of a flask may be stated in liters or cubic centimeters (the mark being *liter*, *l.*, or *cc.*), while all other vessels may be marked only cubic centimeters—*i. e.*, with the mark *cc.* The mark expressing the capacity of a vessel without subdivisions, is placed on the middle part of the body of the vessel.

9. The numbers of the marks on vessels marked for subdivisions of their total capacity, are to be placed at the right end of the lines denoting cubic centimeters as units. These numbers must run consecutively and in only one direction; *i. e.*, either from the top down or from the bottom up.

The " cc." mark is added to the line bearing the largest number, whether it be at the beginning or at the end of the graduation.

10. There must be etched below the mark indicating the capacity, in the case of flasks and other vessels having but one graduation mark, the expression $+15°$ C., indicating the temperature at which the capacity of the flask is equal to the volume indicated by its label. In the case of instruments graduated for fractions of their total capacity, this mark ($+15°$ C.) is etched at least 15 mm. above the graduation. There must also be placed at the left of this mark and at the same height the mark *E.* or *A.*, *Eing.* or *Ausg.*, *Einguss* or *Ausguss*, as the case may be, to indicate whether the instrument has been graduated to hold or to deliver the volume of liquid indicated by its label.

A manufacturer's number, name, and address, and a trade mark may be placed opposite the label mentioned above on the

other side of the flask.   In the case of apparatus graduated for subdivisions the manufacturer's marks are to be placed in long lines at the left of the graduation.

11. In the case of all measuring vessels the reading shall be taken at that point of the wall of the vessel where it is cut by the plane which is perpendicular to the axis of the vessel and at the same time tangent to the meniscus of the liquid at its lowest point.

12. Inflow and outflow tubes, stoppers, etc., must not end in the measuring space of the vessel or extend therein.   The limiting of the measuring space directly by cocks is inadmissible. Beyond the part actually occupied by the liquid to be measured the vessel may be provided with cocks, tubes, expansions made of irregular form, etc., *ad libitum*.

13. In the case of measuring vessels having a delivery tube or point, the latter should be drawn out as thin as stability will permit. and its termination should be smooth and even.   It is permissible to constrict the orifice somewhat.   In the case of burettes of the Gay-Lussac form, the delivery point should be bent back toward the delivery tube, and should be ground obliquely on the under side.

II. Measuring Vessels without Minor Graduation.

(Flasks and pipettes graduated to deliver one maximum volume).

1. Flasks may be made of the following capacities : 2, 1, $\frac{1}{2}$(0.5), $\frac{1}{4}$(0.25), 0.2, 0.1, and 0.05 liter ; pipettes, of any desired capacity from 1 to 200 cc.

2. In the case of both forms of apparatus the part bearing the graduation mark must be cylindrical (see above, I, 5), of uniform section, and transparent.   Moreover, this cylindrical portion must pass over very gradually into the expanded part of the apparatus.

3. In the case of pipettes the suction tubes must be at least 130 mm. long, and the delivery tubes at least 60 mm., but not more than 300 mm. long.

4. The graduation mark must be at least 70 mm. from the upper end of the neck of a flask, and in the case of a pipette at least 100 mm. from the upper end and at least 30 mm. from the bulb.   The mark must extend entirely around the neck of the flask or the suction tube of the pipette.

5. At the point where the graduation mark is placed the internal diameter of the neck of the flask shall not be less than 6 mm., and shall not exceed the following maximum figures given for flasks of each of the sizes admitted for testing :

Capacity of flask. Liters.	Maximum internal diameter of neck. mm.
2	25
1	20
$\frac{1}{2}$(0.5)	20
$\frac{1}{4}$(0.25)	15
0.2	12
0.1	12
0.05	10

In the case of pipettes the suction and delivery tubes must have an internal diameter of not less than $\frac{1}{2}$ mm. and not more than 6 mm.

6. The bottom of the flask may be slightly reentrant. The circumference of the bottom of the flask must form a plane to which the neck of the flask, is perpendicular. The flask must stand solidly on a horizontal surface.

7. The lower limit of the volume of a pipette may be either the end of the delivery tube or a second mark etched thereon at least 30 mm. from the end.

In the case of pipettes without a cock, the delivery orifice must be of such a size that the discharge of the pipette, conformable to I, 3, (*b*), lasts:

12 to 15 seconds when the pipette is of less than 10 cc. capacity.

15 to 20 seconds when the capacity of the pipette is of 10 cc. or more but less than 50.

20 to 30 seconds when the capacity of the pipette is 50 cc. or more but less than 100.

30 to 40 seconds when the capacity of the pipette is 100 cc. or more.

In the case of pipettes provided with cocks, the testing must be made for that setting of the cock which requires the following time for emptying the pipette:

13 to 17 seconds when the capacity of the pipette is less than 10 cc.

16 to 20 seconds when the capacity of the pipette is 10 cc. or more but less than 50.

23 to 27 seconds when the capacity is 50 cc. or more but less than 100.

33 to 37 seconds when the capacity of the pipette is 100 cc. or more.

III. Measuring Vessels with Minor Divisions.

1. The total volume of vessels graduated for subdivisions thereof may have any value between 1 cc. and 1 liter, but for cylinders and burettes shall not be less than 5 cc., and for burettes and pipettes not more than 100 cc.

2. The subdivisions permitted are as follows :

When the total capacity of the apparatus is 1 cc. and up to and including 2 cc., the smallest subdivision is 0.01 to 0.02 cc.

When the total capacity of the apparatus is more than 2 and up to and including 5 cc., the smallest subdivision is 0.05 to 0.02 cc.

When the total capacity of the apparatus is more than 5 and up to and including 10 cc., the smallest subdivision is 0.05 to 0.1 cc.

When the total capacity of the apparatus is more than 10 and up to and including 50 cc., the smallest subdivision is 0.1 to 0.2 cc.

When the total capacity is more than 50 and up to and including 100 cc., the smallest subdivision is 0.2, 0.5, or 1 cc.

When the total capacity is more than 100 and up to and including 200 cc., the smallest subdivision is 1, 2, or 5 cc.

When the total capacity is more than 200 and up to and including 500 cc., the smallest subdivision is 5 to 10 cc.

When the total capacity is more than 500 cc., the smallest subdivision is 10 cc.

3. The measuring space may be limited by lines below as well as above. In the case of pipettes, the upper graduations must be at least 100 mm. from the upper end of the apparatus and at least 50 mm. in other cases. The lower mark of the graduation, in cases where the bottom of the vessel is not the lower limit of the graduation, must be at least 30 mm. from the lower end of the apparatus or from the beginning of the contraction of the body thereof.

4. The numbering is to be done as follows :

(*a*) In case of division into 10, 1, 0.1, or 0.01 cc., every tenth mark is numbered.

(*b*) In case of division into 2, 0.2, or 0.02 cc., every fifth line is marked.

(*c*) In case of division into 5, 0.5, or 0.05 cc., every second or tenth line is marked.

The numbered lines must extend entirely around the vessel. Of the other lines, the fifth in the case " a " and whenever only every tenth line is numbered, and the first line when every second line is numbered, must extend three-fifths of the way around the vessel, while all other lines extend only one-half way around.

All lines not passing entirely around the vessel must be on transparent glass ; any opaque strips for facilitating the reading of the instrument must not be greater in breadth than two-fifths of the circumference of the tube.

5. The distance between two consecutive division marks must not be more than 12 mm., and for measuring cylinders gradua-ted for each 5 cc. or more, not less than 2 mm., while for all

other measuring vessels this distance must not be less than 1 mm.

IV. LIMIT OF ERROR.

1. Measuring vessels without divisions.

For flasks graduated for delivery the error must not exceed the following limits :

Capacity. Liters.	Allowable error. cc.
2	1
1	0.6
0.5	0.3
0.2	0.2
0.1	0.2
0.05	0.1

For flasks graduated to hold the quantities of liquid just named, the allowable error is one-half as great in each case.

For pipettes delivering only maximum quantity, the allowable errors are as follows :

Capacity of pipette. cc.	Allowable error. cc.
1 to 2	0.01
More than 2 to 10	0.02
More than 10 to 30	0.03
More than 30 to 75	0.05
More than 75 to 200	0.1

2. Measuring vessels with divisions—burettes and pipettes.

Maximum capacity. cc.	Allowable error on maximum capacity. cc.
1 to 2	0.01
More than 2 to 10	0.02
More than 10 to 30	0.03
More than 30 to 50	0.05
More than 50 to 100	0.1

In the case of graduated cylinders of the dimensions just given, the allowable error is double that for burettes and pipettes when the instruments are graduated to hold a certain volume, but four times as great as the errors allowed for burettes and pipettes when graduated for delivery or pouring out.

For larger measuring cylinders graduated to hold definite volumes, the allowable errors are as follows :

Maximum capacity. cc.	Allowable error. cc.
More than 100 to 200	0.5
More than 200 to 500	1
More than 500	2

When graduated for delivery or pouring, the allowable errors are just twice as great.

For measuring cylinders graduated to hold a definite volume, the maximum errors for the volumes indicated by ten of the consecutive smallest divisions must on no part of the graduation be greater than as shown below.

1 cc. when the divisions equal 10 or 5 cc.

0.4 cc. when the divisions equal 2 cc.

0.2 cc. when the divisions equal 1 or 0.5 cc.

0.1 cc. when the divisions equal 0.2 or 0.1 cc.

In the case of cylinders graduated for delivery, double these errors are allowed.   In the case of burettes and pipettes graduated to 0.01 to 0.2 cc., the error must not be greater than one-third of the smallest division, and not more than one-fourth of the smallest division in other cases.

V. Stamping.

The official stamp is etched upon flasks immediately over the graduation mark and also over the label.   On pipettes graduated to deliver one maximum volume the official stamp is etched immediately over the upper mark and immediately under the lower mark, when there is one.

In the case of other measuring vessels the official stamp is placed close above the upper mark and close below the lower one ; besides this, the stamp is also placed on the delivery tube, close to its end.

VI. Fees for Testing.

The fees are as follows :

(*a*) For testing and placing the official stamp on measuring vessels without divisions, 30 *pf.* ($0.072).

Measuring vessels having divisions, 80 *pf.* ($0.192).

(*b*) For mere testing, for each complete volume or each mark tested, 10 *pf.* ($0.024).

If a vessel having divisions is tested for more than 5 marks besides the one indicating the total volume, each additional mark tested is charged for at the rate given under *b*.

VII. Place of Testing.

The testing and stamping of measuring vessels will be done by the Normal-Aichungs-Commission until further notice.

KAISERLICHE NORMAL-AICHUNGS-COMMISSION, HUBER.

BERLIN, July 26, 1893.

Supplemental regulations were adopted by the Aichungs-Commission in 1897 as follows :

ADDITIONAL REGULATIONS FOR THE TESTING OF CHEMICAL MEASURING INSTRUMENTS, ADOPTED BY THE KAISER-LICHE NORMAL-AICHUNGS-COMMISSION, JULY 2, 1897.

I. ADDITIONAL FORMS OF APPARATUS ADMITTED FOR TESTING.

In addition to the forms of measuring instruments for exclusive use for chemical analysis of aqueous solutions, mentioned in the notice of July 26, 1893,[1] the following forms will now be accepted for testing :

a. For use in sugar analysis, flasks with two marks and flasks with one mark, or with two marks for a temperature of 20° (Section II).

b. Flasks for use with viscosimeters with two marks for a temperature of 20° (Section III).

c. Flasks with capacities of 150, 300, 350, 400, 450, 550, 600, 650, 700, 750, 800, 850, and 950 cc. (Section IV).

d. Measuring vessels with incomplete graduation (section V).

e. Overflow pipettes (Section VI).

The forms of apparatus mentioned under *a* to *e* shall meet the requirements of the regulations announced July 26, 1893, in so far as the paragraphs here following do not conflict therewith.

II. FLASKS FOR SUGAR ANALYSIS.

1. These flasks must be graduated to hold the volumes indicated by their labels, and may have capacities of 50, 100 or 200 cc. A second mark may be placed above the one which marks the limit of the capacity of the flask. These two marks must be separated at least 10 mm. in the case of 50 and 100 cc. flasks ; and at least 30 mm. in the case of 200 cc. flasks.

Between the two marks the neck of the flask may be enlarged, provided that it is cylindrical for at least 3 mm. above the lower mark and for at least 3 mm. below the upper mark. The capacity limited by these two marks must not be greater than the tenth part, nor less than the two-hundredth part of the capacity of the flask as limited by the lower mark.

2. Besides the label *E,* or *Eing.,* or *Einguss,* the standard temperature, $+15°$ C. or $+20°$ C., shall be etched upon the flask (Section 1, 10, of the regulations of July 26, 1893). The label indicating the capacity of the flask must be etched upon the body of the flask ; and, in the case of flasks with two marks, must denote the capacity of the flask as limited by the lower mark. Flasks with two marks must have, in addition, a label etched midway between the two marks and indicating the capacity of

[1] *Reichs-Gesetzblatt,* Beilage No. 30.

the space included between them, stated in cc. or in fractions of a liter.

3. The internal diameter of the neck of the flask must not be greater than 10 mm. for 50 cc. flasks; not greater than 12 mm. for 100 cc. flasks; and not greater than 25 mm. (15 mm?)[1] for 200 cc. flasks.

4. In the case of flasks with two marks, the upper mark must be at least 50 mm. from the upper end of the neck; in the case of flasks with one mark, the mark must be at least 50 mm. from the upper end of the neck for 50 and 100 cc. flasks, and at least 70 mm. for 200 cc. flasks.

5. The limits of error prescribed by Section IV, 1, of the regulations of July 26, 1893, for flasks graduated to hold 50, 100, and 200 cc. must not be exceeded by sugar flasks of the same respective capacities.

In the case of flasks with two marks, the limit of error of the volume included between the two marks is one-half of that permitted for the entire capacity of the flask.

6. The stamping is to be done in the manner prescribed for flasks at present admitted for verification. In the case of flasks with two marks, however, a second stamp is to be placed above the upper mark. The stamp for the lower mark may be etched directly under the lower mark.

7. The fees will be, in addition to the regular fee of 10 *pf.* for each piece of apparatus presented for verification :

a. For testing and stamping flasks :

　　Flasks with one mark, 40 *pf.* ($0.096) ;
　　Flasks with two marks, 60 *pf.* ($0.144).

b. For mere testing :

　　For each mark tested, 10 *pf.* ($0.024).

III. Flasks for Viscosimetry.

1. These flasks are only to be graduated to deliver the volumes indicated by their labels ; and are to be made only with two marks, one for 200 cc. and one for 240 cc. Between the two marks the neck of the flask may be expanded in the form of a bulb, but it must still be cylindrical for at least 3 mm. above the lower mark and for the same distance below the upper mark.

2. The internal diameter of the neck must not exceed 20 mm. at either mark.

3. In addition, the requirements of Section II, paragraphs 2 and 4 to 7 must be fulfilled with the restriction that the label is to be *A*, or *Ausg.*, or *Ausguss*, and $+ 20°$ C. ; and the limits of error are to be those of flasks graduated for pouring out.

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[1] In the regulations as copied in *Ztschr. angew. Chem.*, this number is 25 mm., while in *Ztschr. anal. Chem.* it is 15 mm. See references above.

IV. Other Flasks.

In view of the additional forms of apparatus admitted for testing by Section I, *c*, the regulations of July 26, 1893, in so far as they refer to flasks, are amended as follows :

Section II, 5. At the point where the graduation mark is placed, the internal diameter of the neck must not be less than 6 mm., and must not be greater than 10 mm for 0.05 l. flasks ; not greater than 12 mm. for 0.1 to 0.2 l. flasks ; not greater than 15 mm. for 0.25 to 0.45 l. flasks ; not greater than 20 mm. for 0.5 to 1 l. flasks ; and not greater than 25 mm. for 2 l. flasks.

Section IV, 1. The positive or negative error for flasks graduated for delivery must not exceed 1 cc. for 2 liter flasks ; 0.6 cc. for flasks delivering from 1 to and including 0.55 liter ; 0.3 cc. for flasks delivering from 0.5 to 0.3 liter ; 0.2 cc. for flasks delivering 0.25 to 0.1 liter ; and 0.1 cc. for 0.05 liter flasks.

In the case of flasks graduated to hold the volumes named, the respective limits of error must not exceed half the amounts named.

V. Measuring Vessels with Incomplete Graduation.

1. The lowest marks of these instruments, which may or may not be provided with a foot, limits an unsubdivided cylindrical or bulb-shaped space having a capacity of a certain number of whole cc.

2. When this lower space is bulb-shaped, that portion of it extending downward from the graduation mark must be cylindrical for at least 15 mm.

If the vessel is enlarged above the upper mark, the enlargement must begin at least 30 mm. from the upper mark.

3. The graduation of these vessels shall be done in the manner described for measuring glasses of forms previously admitted for testing, in accordance with which the number placed opposite the lowest mark indicates the capacity of the ungraduated part. In determining the graduation permissible (Section III, 1 and 2, of the regulations of July 26, 1893), the space included between the upper and lower marks is to be considered the total capacity, but neither this space nor the lower ungraduated space may exceed 100 cc.

4. The stamp placed underneath the lowest mark attests also the accuracy of the ungraduated portion.

VI. Overflow Pipettes.

1. Overflow pipettes are pipettes whose capacities are limited above by the end of the upper tube instead of by a mark placed

thereon. The apparatus may be otherwise constructed like ordinary pipettes, the filling being done by means of the delivery tube; or a special tube for the entry of the liquid to be measured may be provided, both the inflow and outflow tubes being controlled by the same cock.

2. The end of the upper tube must be even; its internal diameter must not be greater than 3 mm. in the case of pipettes delivering 500 cc. or less, and not greater than 5 mm. in the case of pipettes of larger capacity. The upper tube must not be longer than 75 mm.; the lower tube not longer than 150 mm. Overflow pipettes may have any capacity between 1cc. and 2000 cc.

3. The time of emptying of overflow pipettes delivering from 1 to 200 cc. must be the same as the time prescribed for ordinary pipettes of the corresponding capacity; for pipettes delivering more than 200 cc. to 500 cc., the time of delivery must be 55 to 65 seconds; for pipettes delivering more than 500 cc. to 1000 cc., 110 to 130 seconds; and for pipettes delivering more than 1000 cc., 170 to 230 seconds (200 seconds?).[1]

4. The limits of error allowable for overflow pipettes of capacities from 1 cc. to 200 cc. are those prescribed for ordinary pipettes of the corresponding capacities; for pipettes delivering more than 200 cc. to 500 cc., the limit of error allowable is 0.2 cc.; for pipettes delivering more than 500 cc. to 1000 cc., 0.3 cc.; for pipettes delivering more than 1000 cc. to 2000 cc., 0.5 cc.

5. There shall be placed upon overflow pipettes at least three stamps. One of these shall be placed over the label, the second one immediately below the upper end of the upper tube, and the third one on the outflow tube close to its end.

In case the capacity of the pipette is limited below by a mark on the outflow tube, a fourth stamp must be placed immediately under the mark.

6. In addition to the regular fee of 10 pf. ($0.024) for each piece of apparatus presented for verification, the charges for testing, stamping, etc., will be as follows:

    a. For testing and stamping

        Overflow pipettes delivering 200 cc. or less, 40 pf. ($0.096);
        Overflow pipettes delivering more than 200 cc., 60 pf. ($0.144).

    b. For mere testing

        Overflow pipettes delivering 200 cc. or less, 10 pf.($0.024);
        Overflow pipettes delivering more than 200 cc., 30 pf. ($0.072).

[1] The statement in the *Ztschr. angew. Chem.* is 230 seconds; in the *Ztschr. anal. Chem.*, 200 seconds

VII. Place of Testing.

The testing of all forms of measuring instruments named will be done by the Normal-Aichungs-Commission or at the places designated for the testing of chemical measuring instruments in Article 1, Section VII of the notice of April 8, 1896 (Reichs-Gesetzbl. 1896, Beilage zu No. 9).

VIII.

1. The regulations of July 26, 1893, Section II, 4, are hereby amended so that 50 cc. and 100 cc. flasks are allowable with the graduation mark at least 50 mm. from the upper end of the neck.

2. Under Section III, 2, of the regulations of July 26, 1893, the following additional forms of apparatus are provided for :

Instruments having a total capacity of 5 cc. and graduated in 0.1 cc. divisions; and instruments having a total capacity of 10 cc. and 0.02 cc. (0.2 cc?) divisions.[1]

3. The requirements of Section IV, 2, of the regulations just mentioned are amended as follows :

Moreover, the positive or negative error allowable for the capacity limited by each mark, or between two marks must not be greater than one-half of the error permitted for the entire capacity of the instrument, in case the fractional capacity in question is less than one-half the total capacity ; and the error of a fractional capacity equal to or greater than one-half of the total capacity of the instrument must not exceed the error permitted for the total capacity.

The graduation must also appear regular to the eye. In no case may adjacent smallest divisions differ from each other by more than one-fourth of the distance between the lines limiting each of these smallest divisions.

Regulations for the Testing of Instruments for Determining the Percentage Strength of Sugar Solutions.

I. There shall be admitted for testing glass thermo-saccharimeters which indicate the temperature in degrees of the centigrade thermometer, and, at a temperature of $+20°$, the per cent. by weight of sugar contained in pure sugar solutions.

The thermometer scale of the instrument must be divided in whole or in half degrees. When the percentage scale is divided in whole or in half per cent., the thermometer shall be divided in whole degrees and otherwise in half degrees.

The entire length of the divisions of a percentage scale must not exceed 200 mm. ; the length of its smallest subdivisions must be at least 1 mm.

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[1] The statement in the *Ztschr. angew. Chem.* is 0.02 cc. ; in the *Ztschr. anal. Chem.*, 0.2 cc.

Thirty per cent. shall be regarded as the normal range for each instrument. Hence, three kinds of instruments will be necessary : 0 to 30 per cent. ; 30 to 60 per cent. ; and 60 to 90 per cent. Instruments with scales of other ranges are, however, allowable. Instruments with 0.1 per cent. subdivision must not have a greater range than 20 per cent.

The thermometer scales must be made for a range of temperature from 0° to +35°. In the case of instruments graduated for whole or half per cent., the thermometer scale may be extended to 70°. The length of the smallest subdivision of the thermometer scale must be at least 1.5 mm.

II. 1. The loading of the instrument, necessary for maintaining its vertical position when floated in the solution, shall be supplied by the bulb of a thermometer.

Material for making the final adjustment of the instrument may be placed on the inside of the scale, but it must be of such a nature as to make it impossible for it to become loosened by external force or because of its own properties.

2. The outer surface of the instrument shall be regular and symmetrical with respect to its axis ; its proportion shall be such that it assumes a perpendicular position when floated in a liquid.

3. The top of the spindle shall be regularly rounded and have a smooth surface with no depressions or ridges which may hinder the stamping of the instrument.

The external diameter of the body of the instrument must not exceed 28 mm., and that of the spindle must not be less than 4 mm. nor more than 7 mm.

The capillary tube of the thermometer must have no expansion above the scale, and shall only be of such length that the instrument may be heated to 75° C. without danger of breaking.

4. The paper scale must be fastened to the glass wall of the instrument in a permanent manner. Cements which loosen on warming are not permissible.

5. The upper end of the percentage scale shall be at least 15 mm. below the upper end of the spindle.

The upper end of the thermometer scale shall be at least 20 mm. below the place where the glass body of the instrument begins to contract.

6. Upon the percentage scale, in the case of division in whole per cent., the marks for the fifth and tenth per cent. shall be numbered and shall be longer than the others. In other cases the mark for each whole per cent. shall be numbered. In case of divisions for each 0.1 per cent., the marks for each half per cent. shall be longer than the other marks. The shortest marks shall extend at least one-fourth of the way around the spindle.

On the thermometer scale the marks shall run in uninter-

rupted course and shall be visible on both sides of the capillary tube ; those for each fifth degree shall be longer, and those for each one-half degree shall be shorter than the others.

Each tenth degree shall be numbered.

The numbering of the marks and also the labeling of the scales shall be readily legible.

7. The per cent. scale shall extend into the expansion of the spindle leading into the body of the instrument, but shall not extend into the latter ; it may, however, only bear marks so far as the spindle is cylindrical.

The marks of the thermometer scale may extend downward to within 2 mm. of the bend in the capillary tube.

8. The scales must not have appreciable error of division ; adjacent subdivisions must not differ from each other by more than one-fourth of their mean length.

III. The thermometer scale shall bear the label " Degrees of the centigrade thermometer"; and the percentage scale, the label " Percentage-by-weight saccharimeter" (" *Saccharimeter nachs Gewichtspercenten*").

A manufacturer's number shall be placed at the upper end of the thermometer scale.

It is permissible to place the name and address of the manufacturer, and also the date of manufacture on one of the scales, but nothing additional may be placed thereon.

IV. The positive or negative errors permissible are as follows, according as the minor divisions of the percentage scale are for

	1 per cent.	1/2 per cent.	1/5 or 1/10 per cent.
On the thermometer scale ···	0.4°	0.4°	0.2°
On the saccharimeter scale ··	0.5 per cent.	0.25 per cent.	0.1 per cent.

The reading of the thermometer in melting ice must not undergo a greater alteration on heating to the highest temperature of the scale than one-fourth of the limit of error given above for the class of instruments to which it belongs.

On the percentage scale the reading is to be taken at the point where the plane of the surface of the liquid cuts the scale.

V. The official stamp, together with a number and the date shall be etched on the body of the instrument above the thermometer scale. A small stamp shall also be placed at the top of the spindle.

The weight of the instrument in milligrams shall be etched upon the body of the instrument.

Upon the spindle, immediately over the upper end of the percentage scale and immediately below the lowest mark thereof, marks shall be placed which extend at least half way around the spindle. The lower side of the upper mark shall lie in the plane

of the edge of the scale, and the upper side of the lower mark shall be in the plane of the lowest mark of the scale.

VI. In order to obtain true percentage readings the official table of the Normal-Aichungs-Commission must be used.

VII. The following fees have been fixed :

a. For testing and stamping

Each thermo-saccharimeter, 2 *Marks* ($0.48).

b. For mere testing

Of the thermometer scale, 10 *pf.* ($0.024) ;

Of the percentage scale, 25 *pf.* ($0.060).

If more than five points of either scale are tested when an instrument is submitted for testing and stamping, each additional place tested will be charged for at the rates given under *b*.

VIII. The testing of thermo-saccharimeters will be done by the Normal-Aichungs-Commission or by *Aichämter* designated by the Normal-Aichungs-Commission.

KAISERLICHE NORMAL-AICHUNGS-COMMISSION, HOPF.

BERLIN, July 2, 1897.

This act of the Aichungs-Commission, done five years ago, made it comparatively easy for German chemists to obtain volumetric apparatus of known form of construction and of known accuracy. A flask and a burette, tested in accordance with these regulations and bearing the official stamp of the Aichungs-Commission were exhibited at the Boston meeting of this society.

At the International Congress of Applied Chemistry, held in Brussels, in 1894, the question of uniform methods for the analysis of commercial products was discussed, and very naturally the question of international standards for measuring instruments came up at the same time. The following resolutions were adopted unanimously and an international committee was appointed to continue the work and report at the next congress.

"1. The International Congress of Applied Chemistry adopts as the international unit for the graduation and calibration of chemical apparatus, the metric liter and its decimal subdivisions.

"2. It is of the opinion that the centigrade, or Celsius, thermometer should be used to the exclusion of all others.

"3. An international commission, composed of members elected by the congress, shall be entrusted with the duty of determining the conditions of graduation, of testing, and for using chemical apparatus, particularly flasks, burettes, pipettes, and hydrometers of various sorts. This commission shall also fix the temperature at which these instruments shall be graduated. It shall elaborate a table showing the degrees Baumé, Brix, Balling, Vivien, etc., which are equivalent to the various indications of the specific gravity hydrometer ; and shall prepare a

table showing the corrections which are to be applied to the readings of various forms of hydrometers, when these readings are made at other than standard temperatures.''[1]

Preparatory to taking part in the work of the Second International Congress of Applied Chemistry, held in Paris in 1896, the Verein deutscher Chemiker appointed a committee to meet with representatives of the Aichungs-Commission and draft a statement of the German view of the question of standards for chemical measuring instruments.

A. Schmidt, of Cologne, was chosen to present the statement at the Paris congress, as the representative of the Verein deutscher Chemiker, and Prof. Weinstein attended the congress as the representative of the Aichungs-Commission.[2]

This report of the German Committee, changed to accord with the resolutions adopted by the Paris Congress, reads as follows:

PROPOSED REGULATIONS FOR THE CONSTRUCTION AND GRADUATION OF HYDROMETERS AND CHEMICAL MEASURING APPARATUS.

[Zeitschrift für angewandte Chemie, 1896, 603–607.]

A. General Considerations.

1. The unit of volume shall be the true liter and its decimal subdivisions.

2. The basis for the comparison of specific gravities (densities) shall be pure water at $4°$ and under normal pressure.

3. All weight determinations shall be reduced to weights *in vacuo* by use of Regnault's tables.

4. Temperature shall be expressed in degrees of the centigrade hydrogen thermometer of the International Bureau of Weights and Measures.

5. For the normal temperatures for hydrometers and chemical measuring vessels, $0°$, $15°$, $17.5°$ or $20°$ of the above-mentioned thermometer scale may be chosen. Tables shall be prepared by an international commission for the correction of readings to the normal temperatures.

6. Hydrometers and chemical measuring vessels shall be constructed from glass which possesses the greatest possible resistance to the action of the liquids measured. Each instrument must bear a label showing its normal temperature and unit of volume or specific gravity.

7. The length of the intervals between the marks for the smallest subdivisions of the scales of the instruments shall in all cases be greater than 1 mm.

[1] Compte-rendus du congres international de chimie appliqué, Bruxelles-Anvers, 4–11 aout, 1894, pp. 205–206.

[2] *Ztschr. angew. Chem.* (*1896*), 406, 602 ; (*1897*), 519.

8. In making readings at the level of a liquid, consideration must be given to the variation in the phenomena of capillarity.

9. The stems of hydrometers and the graduated parts of measuring vessels must not vary greatly from the cylindrical form.

10. The testing of hydrometers and chemical measuring vessels may be made by comparing them with carefully wrought standards, or by means of the proper weight determinations.

11. In using hydrometers and chemical measuring instruments, the same rules and methods of procedure should be followed as were used in standardizing the instruments.

B. SPECIAL REQUIREMENTS.

(a) *Hydrometers.*

1. The scales of hydrometers may be graduated in units of specific gravity, or of the scales of Baumé, Brix, Balling, etc. For the conversion of the readings of arbitrary scales to the equivalent specific gravity, tables shall be prepared by an inter. national commission.

2. For liquids of various capillary properties, special hydrometers shall be used, each graduated for measuring a certain liquid. Each instrument must bear a label showing for what liquid, or group of liquids of similar capillary properties, it has been graduated. The use of the same instrument for solutions of widely different capillary properties is allowable, if the proper corrections be applied to the readings.

3. Hydrometers shall be read, as a rule, at the point where the plane of the surface of the liquid cuts the stem of the instrument, without regard to the meniscus formed by capillarity. In the case of non-transparent liquids, the readings of a hydrometer which has not been graduated for working under such conditions, must be corrected to the true level of the liquid.

4. Hydrometers shall generally be provided with centigrade thermometers, whose scale shall include the zero point.

5. In order to render it certain that the position of the scale within the instrument does not change, a mark shall be placed on the stem in such a position as to be just opposite one of the limiting marks of the scale when the latter is in its correct position.

6. The maximum limit of positive or negative error of a hydrometer shall not exceed, in general, the smallest division of its scale.

(b) *Chemical Measuring Vessels.*

(The regulations recommended under this head are not essentially different from those of the Kaiserliche Normal-Aichungs-Commission, as given above.)

Francois Dupont read an elaborate report before the Paris congress, as the representative of the committee appointed by the Brussels congress, in the course of which he stated that no meeting of the committee had ever been held. The subject discussed by the congress seems to have been principally that of a standard temperature. A. Schmidt, of Cologne, asked that the question of temperature be left open until the Vienna congress. After a lengthy discussion, participated in principally by Belgian and French chemists, the president suggested a resolution adopting four temperatures, 4°, 15°, 20°, and 30°, with 4° as a reference temperature, and recommending correction tables for each of the four temperatures. This resolution was unanimously adopted.

The resolutions adopted relative to standards for chemical measuring instruments, as published in the official report of the congress, Vol. 5, pp. 227–228, were as follows :

"1. The unit of volume is the metric liter and its decimal subdivisions.

"2. The specific gravity of liquids is to be referred to 4° C., consequently, hydrometers must be graduated in such a manner that they read o or 1.000 when floated in distilled water having a temperature of 4° C.

"3. Tables for comparison of specific gravity with the different hydrometric and saccharometric degrees (Baumé, Brix, Balling, Vivien, Brix-Dupont, etc.), shall be prepared by an international commission. Tables of this sort shall be made for temperatures of 4°, 15°, 20°, and 28° C.

" Tables of corrections shall be prepared by the same commission for temperatures other than those just mentioned.

"4. All weighings shall be reduced to weights in vacuo by means of the tables deduced from the experiments of Regnault.

"5. Temperature should be expressed in degrees of the centigrade hydrogen thermometer, adopted by the International Committee of Weights and Measures.

"All other questions relating to the conditions of construction, graduation, calibration, verification, and reading of chemical measuring instruments shall be referred to the international commission.

"6. The international commission, charged with the duty of preparing tables for the comparison and correction of hydrometer readings, and of establishing regulations for standard measuring instruments, shall be composed of two subcommissions, one French and the other German. The two subcommissions shall communicate with each other and enlist the services of such delegates to the congress as care to participate in the work."

The establishment of uniform and well-defined standards for chemical measuring instruments was thus heartily approved by the

Paris congress ; certain general standards were adopted as land-marks ; and two commissions were created for carrying out the details of formulating international standards.

The German commission was especially active during the interim between the Paris and Vienna congresses, and presented an elaborate report at the latter, being represented by Prof. Weinstein. The recommendations for standards presented at the Paris congress by Schmidt, as the representative of the Verein deutscher Chemiker, were taken up paragraph by para-graph by the Vienna congress and adopted after slight altera-tions. Prof. Weinstein announced progress on the preparation of tables for the density of sugar solutions, acids, mineral oils, etc., at various temperatures, and samples of the tables were presented. These tables will be published privately.

The French commission, through its president, Démichel, presented an essentially concurrent report.

The definition of the relation of Baumé degrees to specific gravity was left to the commissions, which were continued.

A prominent auxiliary feature of the Vienna congress, and one of direct interest in this connection, was the second meeting of the International Commission on Uniform Methods of Sugar Analysis. The work of this commission is especially interest-ing, in view of the controversy now in progress between the U. S. Treasury Department and certain importers of sugars. This litigation involves the regulations governing the testing of sugars and is an excellent illustration of our need of well-defined legal standards for all forms of chemical measuring instruments. At the meeting of the International Commission just mentioned, the United States was represented by Drs. Wiley and Wiech-mann. The work of the commission on the comparison of stand-ard quartz plates, and the influence of temperature on the specific rotation of sucrose, were among the more important topics dis-cussed ; but, from our present point of view, the agreement of the commission to discard the Mohr flask, in favor of the true one-tenth liter flask, is of the highest interest. Hitherto, it has been necessary to keep certain flasks for sugar analysis alone, in lab-oratories which are otherwise equipped with volumetric appara-tus graduated in accordance with the true metric system.[1]

Within a year, Belgian chemists have inaugurated a move-ment in the association with the view of obtaining the coopera-tion of the Belgian Bureau of Standards in the testing of chem-ical measuring instruments, and in the establishment of standards therefore. Their discussions on this subject may be found in the recent issues of the *Bulletin de L' Association Belge des Chimistes*, beginning with the number for December 1898, which con-

[1] Wiley : This Journal, 21, 73.

tains a criticism of the regulations of the Kaiserliche Normal-Aichungs-Commission by L. L. de Koninck.

The regulations of the Kaiserliche Normal-Aichungs-Commission for the construction, graduation, and verification of chemical instruments for measuring volume, while still in a stage of evolution, have stood the test of a five years' trial and the critical examination of three international congresses of chemists who are interested in all refinements of apparatus and methods consistent with practical results. Some criticisms of the minor details of these regulations have been made. Notably, by Dr. Julius Wagner in his "Maassanalytische Studien," published by Oskar Liner, Leipzig, 1898. Dr. H. P. Talbot has very kindly consented to prepare a review of Dr. Wagner's paper for this Journal, and thus bring the criticisms contained therein before the society for consideration. The most serious mistake of the Aichungs-Commission's regulations, namely, the directions for testing the minor divisions of burettes, has been corrected in the supplemental regulations issued in 1897.

There has also been some dissatisfaction among technical chemists concerning the special hydrometer for sugar solutions as constructed and tested in accordance with the Aichungs-Commission's regulations (geaichte saccharimeter). See Weinstein, "Ueber die geaichten Saccharimeter" (*Ztschr. angew. Chem.*, (*1899*), 369–70 ; *Chem. Centrbl.*, (*1899*), I, 1098) and the other articles therein cited written by Göckel, Bruhns, and Classen.

The regulations, as a whole, must be regarded as a long step in advance, and, by their adoption, European chemists have placed themselves in a position to obtain with readiness and without excessive cost, instruments of a high degree of accuracy and of a desirable form of construction. It now remains for American chemists to follow their example.

THE WORK OF AMERICAN CHEMISTS.

The question of the importance of legal standards for measuring instruments has frequently been raised by American chemists, and parties to suits at law and to commercial transactions are almost every day impressed with the need of standards of this kind. The Association of Official Agricultural Chemists seems to have been the first scientific body of this country to undertake seriously the work of improving the quality of our measuring instruments.

In the writer's recommendations of "subjects appropriate for investigation during the ensuing year" at the close of his report as "Reporter on Methods of Sugar Analysis of the Association of Official Agricultural Chemists for 1895," the following words were used : "A comparison of the accuracy of the various

grades of Brix spindles offered for sale by apparatus dealers. A comparison of the accuracy of the graduated glassware offered for sale by apparatus dealers, with the view of prescribing the limits of error allowable in graduated glassware to be used in official work. A similar comparison of the thermometers offered for sale by the dealers.'''[1] No action was taken, however, by the 1895 convention.

At the meeting of the association just named, held in 1896, a committee was appointed to consider the question of standards for volumetric apparatus, standard temperature for specific gravity determinations, etc. This committee, composed of B. W. Kilgore, C. L. Penny, and E. E. Ewell, made a preliminary report to the convention of 1897.[2] The committee was continued and its membership increased to five, G. C. Caldwell and H. W. Wiley being appointed as the additional members.

At the winter meeting of the American Chemical Society, held in Washington, 1897, the writer, acting on the suggestion of Prof. B. W. Kilgore, chairman of the committee of the Association of Official Agricultural Chemists just considered, introduced the following motion : '' That a committee of five be appointed by the president to study and report upon the means by which the society can hasten the adoption of uniform systems of graduation, definite limits of accuracy, and standard methods for using all forms of measuring instruments in use in chemical laboratories. Further, that the committee be instructed to cooperate with other scientific bodies which have undertaken this work, or which may enter upon it in the future.'' This motion was referred to the council, and, after favorable action by that body a committee was appointed, which, after the successive resignations of Profs. Kinnicutt and Venable, is now composed of H. P. Talbot, C. E. Linebarger, G. E. Barton, Louis A. Fischer, and the writer.

The committee was promptly organized by correspondence after its members had been notified of their appointment by the secretary of the society. After much correspondence, it was agreed by a majority vote of the committee that no formal report be made at or previous to the meeting of the society held in Boston, August, 1898. In the meantime, at the suggestion of the chairman of the committee, the president of the society extended a formal invitation to the superintendent of the U. S. Coast and Geodetic Survey to present a paper at the Boston meeting of the society, in which should be described the facilities for standardizing chemical measuring instruments afforded by the U. S.

[1] See the Proceedings of the Twelfth Annual Convention of the A. O. A. C., Bulletin No. 47, Division of Chemistry, U. S. Department of Agriculture, page 154.

[2] See Proceedings Fourteenth Annual Convention of the A. O. A. C., Bulletin No. 51, Division of Chemistry, U. S. Department of Agriculture, pages 137–139 and 159–164.

Office of Standard Weights and Measures and by similar bureaus of foreign governments.

In response to the request, a paper on this subject was presented at the Boston meeting by Mr. Louis A. Fischer, of the Office of Standard Weights and Measures. By a vote of the society, this paper was referred to the Committee on Papers and Publications, with the recommendation that it be published in the Journal, as has been announced by the secretary of the society in his report of the meeting.

At the close of his paper, Mr. Fischer recommended that the society adopt the following definitions of the liter, density, and a degree of temperature :

" 1. The liter, as defined by the International Committee of Weights and Measures ; *viz.*, the volume of the *mass* of a kilogram of pure water at the temperature of maximum density, and under a pressure of 760 mm. of mercury.

" 2. Density, defined as the ratio of the mass of a substance to that of an equal volume of pure water at its maximum density (4° C.).

" 3. The centigrade degree of the hydrogen thermometer of the International Bureau of Weights and Measures."

Mr. Fischer also recommended " that the society adopt some convenient temperature, at which all volumetric apparatus shall contain their stated capacities."' These recommendations were referred to the committee for consideration.

A paper on " Volumetric Apparatus" was read at the Boston meeting by Mr. G. E. Barton, a member of this committee. In the course of his paper, which has already appeared in the Journal, Mr. Barton very clearly shows the need of standards for this class of measuring instruments.[2]

During sessions of the committee held at the time of the Boston meeting of the society, it was voted to limit the work of the committee for the present to the consideration of the proper form, system of graduation, limits of accuracy, manner of labeling, and methods of using volumetric apparatus.

The following motion, further defining the work of the committee for the immediate future, was presented by Prof. F. P. Venable, and adopted by a vote of the committee :

" That the members of the committee take under consideration the reports of the German Commission and the Vienna congress and, after making such corrections or additions as may be agreed upon, use this as a basis for a report to the society."

The writer presented to the committee a somewhat elaborate scheme for securing the cooperation of the members of the society in a study of the quality of chemical measuring instru-

[1] This Journal, 20, 912–927 (*1898*).
[2] *Ibid.*, 20, 731–739 (*1898*).

ments now in use, with the view of increasing the interest in the work of the committee and at the same time obtaining evidence of the directions in which reforms were most greatly needed. As the plan only received the hearty approval of one other member of the committee, it was abandoned.

The committee is now striving to bring before the council at an early date a series of recommendations which include certain definitions of fundamental standards, and the request that the U. S. Office of Standard Weights and Measures adopt regulations governing the construction, calibration, verification, etc., of chemical measuring instruments, as mentioned at the opening of this paper.

As the chairman of the committee, I take this opportunity to announce that the committee will be very glad to answer inquiries or to accept suggestions from the members of the society whenever they may find it convenient to offer them. I shall be especially pleased to see discussions of the subject of standards for volumetric apparatus or for other forms of measuring instruments, presented in this Journal.   ERVIN E. EWELL.

WASHINGTON, D. C., March 7, 1899.

NEW BOOKS.

MAASSANALYTISCHE STUDIEN. Habilitationsschrift. VON Dr. JULIUS WAGNER. Leipzig : Oskar Leiner. 1898. pp. 123.

Since the adoption of the regulations of the Kaiserliche Normal-Aichungs-Commission of Berlin in June, 1893, those regulations have probably been generally accepted as representing the best results of mature thought upon questions relating to practical and desirable accuracy in the graduation and calibration of volumetric apparatus, and the precautions to be taken to ensure the preparation of trustworthy utensils. Committees appointed by three International Congresses have practically adopted the equivalent of these regulations as expressing their views, and only a few minor modifications were adopted by the Aichungs-Commission in 1897. In the little volume under consideration, Part I of which is devoted to general sources of error in volumetric analyses, Dr. Wagner has criticised certain of the conditions prescribed by the Normal-Aichungs-Commission as inadequate, and presents experimental data in support of his statements. This criticism demands some attention at this time, from its close connection with the work of the Committee on Measuring Instruments appointed by the President of the Amer-

ican Chemical Society to consider what steps should be taken, or regulations adopted, to promote uniformity of standards and practice, and greater accuracy of manufacture in connection with measuring utensils.

In the opinion of Dr. Wagner apparatus having the stamp of the Normal-Aichungs-Commission requires reexamination before it can be used in scientific investigations, because the degree of accuracy demanded is less than is attainable in the chemical processes in connection with which it is used, and also less than is practically attainable in manufacture and graduation. Dr. Wagner first refers to Classen's criticism of the regulations of the commission[1] because no account is taken of the variation in the amount of fluid which adheres to the walls of the vessels in the case of fluids of varying character. Dr. Wagner first shows that glass utensils are apparently most readily and completely cleansed by treatment with sulphuric acid and potassium bichromate, and notes the striking fact that a pipette containing a very thin layer of oil on its inner surface delivers more liquid than when thoroughly cleaned. He then studies the behavior of solutions of twentieth-normal bichromate, normal sodium carbonate, of concentrated sulphuric acid, and of several concentrated salt solutions, and determines, by weighing, the volume of the liquid adhering to the burette. His results indicate that the differences lie within the limits of error of observation, except in the case of concentrated sulphuric acid, from which it appears that the criticism of Classen is not well founded.

The first of the measuring instruments discussed is the pipette. Regarding the accuracy to be demanded in the use of pipettes, Böckmann, in his *Chemische Technische Untersuchungen, 1893*, I, 178, places the average value of the allowable error at 2/1000 for volumes from 1 to 25 cc., and 1/1000 from 50 to 2000 cc. This may be regarded as a fair statement of the requirements for technical use; yet, as is pointed out, the Aichungs-Commission's regulations allow a variation of 1/100 for a one cc. pipette; 1/200 for two cc.; 4/1000 for five cc.; 2/1000 for ten cc.; 1/1000 for twenty-five, fifty, and one hundred cc.; a lack of uniformity which may in itself become a source of error.

To indicate the degree of accuracy which might properly be

[1] Mohr's Titrirmethode, 7th Edition, p. 55.

demanded for research work, Dr. Wagner examined fourteen pipettes, varying from 100 cc. to 10 cc. capacity, and finds that the contents of a pipette may be determined to 2/10000 of its value for pipettes larger than ten cc., and probably to 4/10000 for ten cc. and five cc. pipettes, and that the error arising from the use of a pipette need not exceed these amounts. These quantities are much less than the limits set by the Aichungs-Commission, and a regraduation of instruments tested by this commission is therefore essential for work of high accuracy.

Regarding the method of emptying a pipette, whether by allowing the liquid to run freely, and, at the expiration of a definite time, touching the tube against the side of the vessel, or by gently blowing out the last drop, the data obtained by Wagner are not conclusive, as no advantage is evident on the side of either method. The differences are within the errors of observation. Convenience seems to favor the removal of the liquid by blowing.

But the question may properly arise, whether it is practicable to graduate burettes with an exactness corresponding to that which has just been stated to be attainable in measuring their contents. This, it is stated, may be done, if the restrictions as to the internal diameter of the tubes are suitably made. The Aichungs-Commission demands, in general, that the internal diameter of the tubes shall not be less than five-tenths mm. nor more than six mm. but without further specifications. The position of the mark cannot be accurately fixed within five-tenths mm. while a greater variation is not infrequent, and pipettes are found on the market with tubes so large as to make this uncertainty in marking a source of considerable error. On the other hand, a diameter of five-tenths mm. is so small as to make the use of a pipette annoyingly tedious. A table is given showing the allowable internal diameter in order that the error in marking may not cause an error in volume exceeding 3/10000, the adoption of which would add to the concreteness of the Aichungs-Commission's regulations. In the opinion of Dr. Wagner, the requirements of the Commission that at the orifice the walls of a pipette shall be drawn out as thin as is practicable tends to produce a capillary opening, which is undesirable; this fact leads him to favor blowing out the last drops of liquid as a method of emptying the pipettes now on the market.

Dr. Wagner notes great inequality in practice as regards the time of drainage. He recommends that pipettes should be so constructed with respect to the size of the orifice, that the time of outflow shall be sufficiently long to avoid any after-drainage, rather than to empty the pipette rapidly and to wait for a definite interval. He makes certain statements as to the time necessary to accomplish this.

A similar irregularity in allowable error to that noted in the requirements regarding pipettes is found with respect to measuring flasks, and it is pointed out that, for a variation of one mm. in the position of the mark, the maximum diameter allowable in 500 cc. and 50 cc. flasks as stated by the Commission should be reduced from twenty and ten mm. to fourteen and eight mm. respectively, in order to conform to the allowable variation in cubic centimeters, as stated in the very same regulations of the Commission. Measuring flasks may apparently be read with an accuracy about five times as great as that demanded by the Commission's regulations, with respect to graduation. The author believes that the manufacturers would welcome more explicit statements regarding the allowable variations in the diameter of the necks of the flasks.

Following a discussion of the limit of error in burette readings, the author points out inconsistencies similar to those already noted in the limit of accuracy demanded for burettes by the Aichungs-Commission's regulations, and points out that by suitably limiting the diameter of the burette, uniform accuracy is attainable. Burettes containing fifty cc. should have a diameter of ten to eleven mm., those of thirty cc. eight to ten mm., ten cc. graduated pipettes, five to seven mm. Assuming a necessary minimum error of one-tenth mm. in reading the position of the meniscus, the percentage error is always less than $1/1000$, if the above dimensions are adhered to.

The original statement in the Commission's regulations regarding the allowable error in the small divisions of a burette seems to have been unsatisfactory, and was revised in 1897 but in such a way that, according to Dr. Wagner, it is satisfactory with respect to accuracy, but almost impossible to execute, and he recommends that, instead of striving to attain unreasonable exactness, each burette be accompanied by a table of corrections

(a request made by the Verein Deutscher Chemiker, but set aside by the Commission without assigned reason), or that the results of the calibration be written upon the burette itself.

The Commission places the time to be allowed for a burette to drain at two minutes, but the author regards it as a more advantageous and less time-consuming practice to allow the liquid to run out at the rate of ten cc. in about ten seconds, in which case the reading may be taken at once without appreciable error.

As a result of his work Dr. Wagner makes these recommendations regarding the graduation and calibration of measuring vessels : (1) That they be divided into grades, with respect to accuracy, and that the grade to which each instrument belongs be plainly marked upon it; (2) that the highest grade for pipettes and measuring flasks include only those accurate within 5/10000 of their capacity ; and (3) that, since burettes cannot be graduated with an exactness corresponding to the accuracy desired for scientific work, they should be so calibrated as to assure accuracy within one-tenth mm. at any point of measurement, and that the value of each individual cubic centimeter shall be tested.

The sources of error connected with the process of weighing are next considered and, assuming, in general, an accuracy of one part in one thousand as attainable in analysis, it appears that the reduction of weighings in air to those *in vacuo* is not requisite, since the error is less than the fraction just named. Following this discussion a warning is sounded against the acceptance of reagents of ''guaranteed'' purity as reliable ; the methods of testing reagents are also discussed, and Krauch's *''Die Prüfung der chemischen Reagentien auf Reinheit''* is severely criticised. The closing pages of this part of the volume are devoted to a consideration of the influence of temperature-changes upon the accuracy of volumetric work. It appears that, in general, decinormal solutions may be regarded as having a coefficient of expansion equal to that of water, but solutions of greater concentration require special tables of corrections ; a few values for such solutions are given in this work. The author advocates the adoption of 20° C. as a standard temperature for calibration, rather than 15° C. as named in the Aichungs-Com-

mission's regulations, considering the higher temperature to be more convenient for laboratory use.[1]

Part II of the dissertation is devoted to methods of standardization employed in iodimetry. The conclusions arrived at may be summed up as follows : (1) That the standardization of a thiosulphate solution may be made accurate to one-tenth per cent.; (2) that the best of the bichromates, iodates, and bromates found in the market are very likely to be impure ; and (3) that the presence of potassium bichromate promotes the oxidation of hydriodic acid by atmospheric oxygen and by interfering with the end-point introduces a possible error when the bichromate is used for standardizing purposes.

Part III presents the results of study of the reaction between potassium permanganate and hydrochloric acid, under the influence of certain substances exerting a catalytic influence. Dr. Wagner sums up his results as follows : (1) The decomposition of permanganate in iron titrations in the presence of hydrochloric acid is the result of the intermediate formation and oxidation of a ferrohydrochloric acid ; (2) other salts, such as those of chromium, cadmium, as well as gold and platinum chlorides, cause the same decomposition ; (3) platinohydrochloric acid was found to be oxidized more readily than hydrochloric acid ; (4) by means of cryoscopic methods the existence and gradual formation of a cadmiohydrochloric acid was indicated ; (5) the presence of barium chloride with ferrous salts, causes an essential increase in the decomposition of the permanganate, amounting even to forty-five per cent.; (6) in many chemical changes secondary reactions may take place, without, however, as in the case of real catalysis, increasing the speed of the primary reaction. The secondary reactions seem then to add their effect to that of the primary reaction. Dr. Wagner proposes the term '' Pseudo-Katalysen'' to indicate reactions of this character.

The dissertation is marked by a somewhat aggressive spirit of criticism, but it contains much which bears evidence of careful thought and labor, and is well worth perusal.

H. P. TALBOT.

[1] The regulations of the Normal-Aichungs-Commission have also been criticised by Professor L. L. de Koninck in an article entitled '' Observations relatives aux conditions du contrôle des appareils de mesure en volume par la Commission d' étallonnage normal d'Allemagne,'' published in the *Bull. de l' Assoc. Belge des Chemistes, Dec., 1898.*

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CORRECTION.

In the March number, 1899, page 259, line 20 from top, for "0.3081 gram and 0.2997 gram, from each," read "0.0308 gram and 0.0300 gram, average of several."